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Canadian Water Quality Guidelines for the Protection of Aquatic Life: Inorganic Fluorides

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Canadian Water Quality Guidelines for the Protection of Aquatic Life: Inorganic Fluorides

Report No. 1-1

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This particular issue provides the scientific supporting information and rationale for the development of Canadian Water Quality Guidelines for the protection of aquatic life for inorganic fluorides. The information in this document is current as of 2000, when the document was originally prepared. Minor revisions and editorial changes have been made for publication in 2001. For additional information regarding these guidelines, please contact:

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Canadian Water Quality Guidelines are approved by the Water Quality Guidelines Task Group of the Canadian Council of Ministers of the Environment (CCME). Environment Canada acts as the federal representative and serves as the technical secretariat to this Task Group. These guidelines are included as a 2001 update to the *Canadian Environmental Quality Guidelines*, which was published by the CCME in October of 1999. For CCME publications, please contact:

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This scientific supporting document is available in English only. A factsheet is also available in English under the title *Canadian Environmental Quality Guidelines* (CCME 1999). Ce document scientifique du soutien n'est disponible qu'en anglais avec un résumé en français. Un feuillet d'information est aussi disponible en français sous le titre *Recommandations canadiennes pour la qualité de l'environnement* (CCME 1999).

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Parts of this work are based on that by Warrington (1990) and Environment Canada (1994).

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ABSTRACT

This report presents the Canadian Water Quality Guidelines for the protection of aquatic life for inorganic fluorides. It includes the details of guideline derivation as well as scientific supporting information including chemistry, sources in the environment, releases to the environment, environmental fate and behaviour, and toxicity to aquatic life.

The report focuses on four inorganic fluorides which are of environmental importance: hydrogen fluoride (HF), calcium fluoride [fluorite or fluorspar; (CaF_2)], sodium fluoride (NaF), and sulphur hexafluoride (SF_6). These four inorganic fluorides have varied uses in Canada: in the production of aluminium; as a flux in steel, glass, and enamel production; in drinking water fluoridation; and as an insulation and current interruption medium in electrical switchgear, among many others. Inorganic fluorides are a major by-product of the phosphate fertiliser industry. The total estimated annual release of inorganic fluorides from anthropogenic sources to the Canadian environment (air, land, and water) is in excess of 12 400 tonnes per year. Concentrations of inorganic fluorides in fresh waters across Canada average 0.05 mg F^-/L (ranging from 0.01 to 11.0 mg F^-/L). Marine waters have higher fluoride concentrations than fresh water with a mean inorganic fluoride concentration of 1.3 mg F^-/L (ranging from 1.0 to 1.7 mg F^-/L). Levels of inorganic fluorides in groundwater vary considerably (0.02 to 15 mg F^-/L) depending on the hydrogeological characteristics of the underlying bedrock.

The fate of inorganic fluorides in the atmosphere is influenced primarily by vaporisation, aerosol formation, wet/dry deposition, and hydrolysis. In water, inorganic fluorides remain dissolved in solution under acidic conditions, low hardness, and the presence of ion-exchange material (*e.g.*, bentonite clays and humic acid), calcium or aluminium ions. Fluorides are important for mobilising aluminium into soluble complexes. In acidic waters of pH 5 or lower, fluorides are almost entirely complexed with aluminium.

Inorganic fluorides are taken up by aquatic animals principally through food ingestion. Approximately 99% of the body burden of fluorides is accumulated in bones and teeth, but a small percentage can also be accumulated in soft tissue. Inorganic fluorides taken up by aquatic plants are accumulated in cells and cell walls, causing chlorosis, peripheral necrosis, leaf distortion and malformation. In nature, there is no evidence of biomagnification of inorganic fluorides through the food chain.

Inorganic fluorides act as enzyme inhibitors and have wide-ranging effects. Adverse effects observed in aquatic organisms include: changes in blood composition; reduced size and growth; slowed embryonic and developmental life stage; impaired reproduction; and abnormal or impaired behaviour (*e.g.*, fish migration). Inorganic fluorides are also neurotoxic, causing adverse effects on the central nervous system. Inorganic fluoride toxicity is negatively correlated with water hardness (calcium) and positively correlated with temperature. Several environmental factors can protect against inorganic fluoride toxicity, including calcium, magnesium, selenium, and chlorides.

An interim water quality guideline of 0.12 mg F^-/L is recommended for the protection of all stages of freshwater life against the adverse affects of total inorganic fluorides. It was derived by multiplying the lowest value from an acute, static toxicity study on the net-spinning caddisfly, *Hydropsyche bronta*, a LC_{50} of 11.5 mg F^-/L, by a safety factor of 0.01. The guideline was derived from an acute study, as no acceptable lower value from

a chronic toxicity study was available. Due to a lack of required toxicity studies, neither a full nor an interim water quality guideline for the protection of marine life could be developed at this time.

RÉSUMÉ

Le présent rapport contient les Recommandations pour la qualité des eaux au Canada concernant les fluorures inorganiques en vue de la protection des organismes aquatiques. Il comprend des renseignements sur l'établissement des recommandations ainsi que des données scientifiques justificatives, notamment les paramètres chimiques, les sources de ces composés dans l'environnement, les émissions, le destin et le comportement de ces produits dans l'environnement, ainsi que leur toxicité envers les organismes aquatiques.

Le rapport porte sur quatre fluorures inorganiques qui ont une importance écologique: le fluorure d'hydrogène (HF), le fluorure de calcium [fluorite ou fluorine; (CaF_2)], le fluorure de sodium (NaF) et l'hexafluorure de soufre (SF_6). Ces quatre fluorures sont utilisés à différentes fins au Canada, notamment: production d'aluminium; flux pour la production d'acier, de verre et d'émail; fluoruration de l'eau potable; et milieu isolant et d'interruption du courant dans les appareillages de commutation électrique, entre autres. Les fluorures inorganiques sont un sous-produit important de l'industrie des engrais phosphatés. Au Canada, le total des rejets de fluorures inorganiques d'origine anthropique dans le milieu (air, sol et eau) est évalué à plus de 12 400 tonnes par année. Les concentrations de fluorures inorganiques dans les eaux douces au Canada s'établissent en moyenne à 0,05 mg F^-/L (0,01 - 11,0 mg F^-/L). Dans l'eau salée, les concentrations de fluorure sont plus élevées que dans l'eau douce, la concentration moyenne de ces composés étant de 1,3 mg F^-/L (1,0 à 1,7 mg F^-/L). Les teneurs de fluorures inorganiques dans l'eau souterraine varient énormément (0,02 à 15 mg F^-/L) selon les propriétés hydrogéologiques du substratum rocheux.

Le destin des fluorures inorganiques dans l'atmosphère dépend surtout de la vaporisation, de la formation d'aérosol, des dépôts humides et secs et de l'hydrolyse. Dans l'eau, les fluorures inorganiques demeurent en solution dans les conditions suivantes: milieu acide, faible dureté et présence de matière échangeuse d'ions (p. ex. argiles bentonitiques et acide humique), d'ions calcium ou aluminium. Le fluor est important pour la mobilisation de l'aluminium dans des complexes solubles. dans des eaux acides à pH $\leq$ 5, le fluor est presque entièrement complexé à l'aluminium.

L'ingestion de nourriture est la principale voie d'entrée des fluorures inorganiques chez les organismes aquatiques. Environ 99 % de la charge corporelle de fluor est accumulée dans les os et les dents, mais un faible pourcentage peut aussi s'accumuler dans les tissus mous. Les fluorures inorganiques fixés par les végétaux aquatiques s'accumulent dans les cellules et les parois cellulaires et provoquent différents symptômes (chlorose, nécrose périphérique, déformation et malformation foliaires). Dans la nature, la bioamplification de fluorures inorganiques dans la chaîne alimentaire n'a pas été démontrée.

Les fluorures inorganiques agissent comme inhibiteurs enzymatiques et ont des effets variés. Parmi les effets néfastes observés chez les organisme aquatiques, on peut mentionner des modifications de la composition du sang, une diminution de la taille et de la croissance, un ralentissement du développement de l'embryon et des stades de développement, une perturbation de la reproduction et un comportement anormal ou altéré (p. ex. migration des poissons). Les fluorures inorganiques sont également neurotoxiques et ont des effets néfastes sur le système nerveux central. Il existe une corrélation négative entre la toxicité de ces composés et la dureté de l'eau (calcium) et

une corrélation positive avec la température. Plusieurs facteurs environnementaux peuvent protéger contre la toxicité des fluorures inorganiques, notamment le calcium, le magnésium, le sélénium et les chlorures.

Une recommandation provisoire pour la qualité de l'eau de 0,12 mg F^-/L est préconisée pour la protection de tous les stades de vie dulcicole contre les effets néfastes des fluorures inorganiques totaux. Elle a été établie en multipliant la valeur de CL_{50} la plus faible tirée d'une étude de toxicité aiguë sans renouvellement menée sur l'espèce d'Hydropsychidae, le *Hydropsyche bronta*, de 11,5 mg F^-/L par un facteur d'incertitude de 0,01. La recommandation a été établie à partir d'une étude aiguë, car aucune valeur faible acceptable provenant d'une étude de toxicité chronique n'était disponible. Faute d'études de toxicité requises, l'établissement d'une recommandation complète ou provisoire pour la qualité de l'eau en vue de la protection des organismes marins n'a pu être effectuée.

1. INTRODUCTION

Canadian environmental quality guidelines (EQGs) are developed under the auspices of the Canadian Council of Ministers of the Environment (CCME) using formal protocols to provide nationally consistent, scientifically defensible approach for assessing and managing toxic substances in the environment. This report elaborates the Canadian Water Quality Guideline (WQG) for inorganic fluorides for the protection of aquatic life. In general, water quality guidelines (WQGs) are used by provincial, territorial and federal agencies to evaluate water quality issues and manage competing uses of water. These guidelines do not constitute values for uniform national water quality as their use will require consideration of local conditions (*i.e.*, site specific usage).

The guideline value for inorganic fluorides is a numerical limit intended to protect all forms of aquatic life and all aspects of aquatic life cycles, including the most sensitive life stage of the most sensitive species over the long term. In this document, background information on inorganic fluorides regarding production and uses, sources and pathways for the entry of fluorides into the Canadian environment, and environmental fate and persistence is based on earlier Canadian assessments by Warrington (1990) and Environment Canada (1994). Background material was updated when relevant new information was available. A comprehensive assessment of the toxicity of fluorides to aquatic life was carried out to evaluate environmental hazards posed by these chemicals. Together, this information was used, in accordance with "A protocol for the derivation of water quality guidelines for the protection of aquatic life", (CCME 1991) to derive numerical a WQG for aquatic organisms. The guideline is based on the most current, scientifically defensible toxicity data available for inorganic fluorides. Though information for both freshwater and marine systems is included herein, sufficient data exists to derive a guideline value to protect freshwater species only.

2. IDENTITY OF SUBSTANCE

2.1 Chemistry and Speciation of Fluorine and Fluorides

Fluorine (F) is a halogen (group VII element) that exists under standard conditions (*i.e.*, room temperature and normal vapour pressure) as a light yellow-green, pungent, acrid gas. Fluorine (CAS 7782-41-4) has the atomic number 9 and a molecular weight of 18.998 g/mol. It is the most electronegative element in the Periodic Table (Neumüller 1981). Ionic fluoride (F^-) is either free or matrix-bound in minerals or covalently bound in inorganic compounds (*e.g.*, hydrogen fluoride) or organic compounds (*e.g.*, freons); all fluorine containing compounds are called fluorides (Whitford 1989; Government of Canada 1993).

Fluorine is an isotopic element, existing nearly exclusively as only one natural stable isotope (^{19}F). The longest-living radioactive fluorine isotope is ^{18}F, with a half-life of 109 minutes and 48.5 seconds. Other radioactive isotopes (^{17}F, ^{20}F, ^{21}F and ^{22}F) are much shorter-lived, with half-lives varying from seconds to a few minutes. Because the electronic configuration of fluorine is $1s^2 2s^2 2p^5$, fluorine needs to gain only one electron in its outer shell to attain an inert noble gas structure to form a very stable inorganic fluoride ion (F^-). Fluorine is exclusively univalent. In many compounds, the stereochemistry of the fluoride ion resembles that of O^{2-} and OH^-, and the ionic radii are similar (F^- 133 pm; O^{2-} and OH^- 140 pm; Cl^- 184 pm; atomic radius of fluorine is 0.71 pm) (O'Donnell 1975).

The great reactivity (*i.e.*, oxidising capacity) of F is due to its high electronegativity, its unusually low dissociation energy (in relation to other halogens), and the great bond strength of its compounds. Fluorine compounds (*i.e.*, fluorides) are characterised by an oxidation state of -1. As the most reactive element, fluorine reacts vigorously with every other element except the inert gases helium, neon, and argon. Fluorine combines also with xenon under mild conditions to form crystalline xenon fluorides. These characteristics are a reflection of the outer electron structure, small size of the atoms, and the weak F-F bond, which is due to the appreciable internuclear repulsion and the electron-electron repulsion of the ion-pairs as a consequence of the close proximity of the two fluorine atoms. The most spectacular aspect of this chemistry is the ability of the strongly oxidising fluorine to bring out abnormally high oxidation states in elements (*e.g.*, BiF_5, IF_7, PtF_6, AgF_2, TbF_4, PuF_6, and CmF_4) (O'Donnell 1975).

Although no spectral absorption bands have been observed for fluorine, continuous absorption occurs at wavelengths below 410 nm with a maximum at about 280 nm (O'Donnell 1975). Other important physical and chemical properties of fluorine are given in Table 1.

Table 1. Physical and Chemical Properties of Fluorine

Property	Value
Atomic number[a]	9
Molecular weight[b]	18.9984032 g/mol
Valence[b]	1
Elemental state[b]	F, gaseous
Physical state (@ 25 °C)[c]	gas
Melting point (F_2)[c]	-219.61 °C
Boiling point (F_2)[c]	-188.13 °C
Specific gravity[b,d]	1.5127 @ -188.13 °C (liq)
Density	1.696 @ 0 °C (liq)
Atomic radius (F)[a]	0.71 pm
Ionic radius (F^-)[a]	133 pm
Electronegativity[b]	4.0
Ionisation energy[a]	1680.6 kJ/mol
Electron affinity[a]	332.6 kJ/Amol
Colour[c]	pale yellow, yellow-green
Odour[c]	strong, choking, intense
Odour threshold[c]	0.035 µg F^-/g
Toxicity by inhalation[c]	1 µg F^-/g (threshold limit value)
Short-term inhalation limit[c]	0.5 µg F^-/g for 5 min
Latent heat of vaporisation[c]	1.67×10^5 J/kg (=71.6 Btu/lb =39.8 cal/g)
Critical pressure[b]	55 atm
E° (calc.)($^1/_2F/F^-$)[f]	2.866
Index of refraction[f]	1.000195

Source:
[a]Greenwood and Earnshaw (1984)
[b]Merck Index (1996)
[c]Hazardous Chemicals Data Book (1986)
[d]Neumüller (1981)
[e]O'Donnell (1975)
[f]Lide (1992)

The abundance of inorganic fluorides in the environment is increasing because of their growing use in industrial and dental health products. Based on levels of inorganic fluorides in ambient air, drinking water, food, and household and dental products, the average total daily intake by humans is approximately 20% below the level at which adverse effects upon the skeleton are expected (Liteplo et al. 1994).

Canadian water quality guidelines for inorganic fluorides are based on the evaluation of four inorganic fluorides with importance in the environment: hydrogen fluoride (HF); calcium fluoride [fluorite or fluorspar; (CaF_2)]; sodium fluoride (NaF); and sulphur hexafluoride (SF_6). Calcium fluoride (CaF_2), cryolite (Na_3AlF_6), topaz ($Al_2(F,OH)_2 \cdot SiO_4$), and apatite ($Ca_5(F,OH)(PO_4)_3$) are among the main industrial and commercial fluoride-containing minerals.

In nature, hydrogen fluoride (HF; molecular weight 20.01 g/mol; density 0.991 g/L) is the most reactive form of fluorine. It is a colourless, pungent, acrid liquid or gas at room

temperature with a melting point of -83°C and boiling point of 19.54°C. It is highly soluble in many organic solvents and water, where it forms hydrofluoric acid (Neumüller 1981; Weast 1985). It is an important industrial compound, with an annual world consumption in excess of 1 million tonnes (Greenwood and Earnshaw 1984); its annual Canadian use is about 70 000 tonnes (Environment Canada 1993). Hydrogen fluoride is manufactured from calcium fluoride and is mainly used in the production of synthetic cryolite, aluminium fluoride, motor gasoline alkylates, and chlorofluorocarbons (CFCs) (CIS 1996).

Calcium fluoride (CaF_2; molecular weight 78.08 g/mol) is a colourless solid with a melting point of 1 403°C and boiling point of 2 513°C. It has a water solubility of 15 mg/L (18°C) and is relatively insoluble in dilute acids and bases (Neumüller 1981; Merck Index 1996). The annual Canadian consumption of calcium fluoride is 92 822 tonnes (Natural Resources Canada 2001). Calcium fluoride is used as a flux in steel, glass, and enamel production, and as the raw material for production of hydrofluoric acid and anhydrous hydrogen fluoride (Neumüller 1981), as well as a molten electrolyte for the separation of oxygen and alumina (Al_2O_3) in aluminium production. Another important calcium- and fluoride-containing mineral, fluoroapatite [calcium hydroxyl phosphate; $(Ca_5(F,OH)\cdot(PO_4)_3]$, is used as a source of phosphates in the fertiliser industry (Neumüller 1981).

Sodium fluoride (NaF; molecular weight 41.99 g/mol) is a colourless to white solid that is moderately soluble in water (42.2 g/L), with a melting point ranging from 988 to 1 012°C and boiling point of 1 695°C (Neumüller 1981). It is usually prepared from hydrofluoric acid and sodium carbonate or sodium hydroxide (Neumüller 1981). The total annual Canadian use of sodium fluoride is unknown. Sodium fluoride is used in drinking water fluoridation, as a preservative in glues, glass and enamel production, and as a flux in steel and aluminium production (Neumüller 1981). Sodium fluoride is currently also registered for use as a wood preservative in Canada. In 2000, 12 tonnes of NaF were used for this purpose. Nearly all of this amount came from sales of a wood preservative paste applied to the groundline portion of in-service utility poles (Muchow 2001, Osmose Inc., pers. com.). The only registration for sodium fluoride as an insecticide expired December 2000 (PMRA 2000, pers. com.).

Sulphur hexafluoride (SF_6; molecular weight 146.05 g/mol; density 6.16 g/L [at 20°C]) is a colourless, odourless, tasteless, chemically inert and non-flammable gas (Neumüller 1987). Its melting point is reported as -50.5°C, and its sublimation point as -63.8°C (Weast 1985; Neumüller 1987). Sulphur hexafluoride is only slightly soluble in water, but is readily soluble in ethanol and bases (Weast 1985). It absorbs strongly in the infrared region around 10 µm (Chu 1991) and is, therefore, flagged as a potential greenhouse gas. The annual imports of SF_6 to Canada are in excess of 110 tonnes (Environment Canada 1993). It is extensively used as an insulation and current interruption medium in electrical switchgear such as power circuit breakers, compressed gas transmission lines, and various components in substations (James 1992; Environment Canada 1993). It is frequently used as a protective inert gas over molten metals such as magnesium and aluminium (Neumüller 1987). Magnesium production in Canada consumes over 90% of imported total SF_6, the remainder of which is used in electronic switchgears. These uses are considered to be non-destructive to SF_6 (Environment Canada 1993).

Some of the physical and chemical characteristics of fluorine-containing compounds are presented in Table 2.

Table 2. Physical and Chemical Characteristics of Fluorine-Containing Compounds

Name of Substance	Empirical Formula	Molecular Weight (g/mol)	Solubility	Melting Point (°C)	Other Properties
Aluminium fluoride	AlF_3	83.98	Sparingly soluble in water; Forms hydrates AlF_3 at n H_2O; where n = 1,3,9	1290	Forms a variety of complexes and adducts
Calcium fluoride	CaF_2	78.08	Sparingly soluble in H_2O (0.015 g/L)	1403	Colourless solid
Fluoroapatite	$Ca_5(F,OH)(PO_4)_3$	504.30	-	-	Hexagonal crystals; green, white, yellow, red, brown, and blue colour; specific gravity 1-3.35; hardness 5
Hydrogen fluoride	HF	20.01	Very soluble in H_2O and many organic solvents	-83.6	Colourless gas or liquid (b.p. 19.54°C); fumes in air; very acrid
Hydrofluoro-silicic acid	H_2SiF_6	144.08	Soluble in H_2O	60-70% solution solidifies at about 19	Exists only in aqueous solution; anhydrous form dissociates into HF and SiF_4
Sodium fluoride	NaF	41.99	Soluble in H_2O (42 g/L)	993	Crystalline powder
Sodium hexafluoro-silicate	Na_2SiF_6	188.06	Soluble in H_2O (6.52g/L)	Decompose s	White granular powder
Sulphur hexafluoride	SF_6	146.05	Readily soluble in ethanol and bases	-50	Colourless gas

Source: Lide (1992)

No information is available on the speciation of inorganic fluorides in fresh waters and biota. The speciation of inorganic fluorides in sea water is 50% F^-, 47% MgF^+, 2.1% CaF^+ and 1.1% NaF^o (Miller and Kester 1976). In fluoridated drinking water, inorganic fluorides exist as the free anion (F^-), whereas in plant and animal tissues, inorganic fluorides exist in both ionic and non-ionic forms (Whitford 1989). Table 3 presents the percentage by weight of fluorine in some inorganic fluoride salts and their solubility in water.

Table 3. Percentage by Weight of F^- in Some Inorganic Fluoride Salts and Solubility in Water at 0-25°C

Fluoride Salt	Molecular Weight (g/mol)	% F[a]	Solubility in Water (0-25°C) (mg/L)
BaF_2	175.33	21.67	1 200
$BaSiF_6$	279.41	40.79	260
CaF_2	78.08	48.67	16 (at 18°C)
$CaSiF_6$	182.16	62.58	Slight; almost insoluble in cold water
HF	20.01	94.96	Soluble[b]
KF	58.10	32.7	923 000 (at 18°C)
K_2SiF_6	220.27	51.75	1 200
KF·HF	78.1	48.7	410 000
LiF	25.94	73.25	2 700 (at 18 °C)
$Li_2SiF_6 \cdot 2H_2O$	191.99	59.37	730 000
MgF_2	62.30	60.96	76 (at 18°C)
$MgSiF_6$	166.38	68.51	650 000
MnF_2	92.93	40.89	6 600 (at 40°C); 4 800 (at 100°C)
NaF	41.99	45.24	42 200 (at 18°C)
Na_2SiF_6	188.06	60.61	6 520 (at 17°C)
Na_3AlF_6	209.94	54.29	-
NaF·HF	62.0	61.3	Soluble[b]
NH_4F	37.04	51.30	1 000 (at 0°C)
$(NH_4)_2SiF_6$	178.15	63.99	181 600 (at 17°C)
$NH_4F \cdot HF$	57.05	66.6	Soluble[b]
SF_6	146.05	78.01	Slight
SrF_2	125.73	30.22	110 (at 0°C)

Source: Neumüller (1987); Lide (1992)
Note:
[a]Calculated
[b]Soluble means virtually unlimited solubility

2.2 Analytical Methods

As there is an abundance of literature dealing with the chemical analysis of inorganic fluorides, but no general overview available in the literature, a review of various analytical methods is summarised in Appendix A.

Measurement of inorganic fluorides in environmental samples are restricted to detecting the free anion (F^-). The ability to distinguish between different chemical species is limited. In the majority of cases, sample pre-treatment is necessary to free the complexed and masked inorganic fluorides, and to convert the matrix-bound fluorides into the free anion, and thus, permit the measurement of total fluorides of the sample. The most commonly used analytical method to measure the free anion is the fluoride ion-selective electrode (F-ISE). Modifications in sample preparation and instruments can influence the sensitivity and recovery, and detection limit. Typical detection limits of the F-ISE for inorganic fluorides range from 0.1 - 300 ng F^-/m_3 (air), 1 - 1000 µg F^-/L (water),

and 0.05 - 20 mg F^-/kg (organic tissues, wet weight). Other methods that may be used to measure the fluoride ion include colourimetry, ion chromatography, atom absorption spectroscopy and photon activation (Neumüller 1981; ATSDR 1991).

3. RELEASE TO THE ENVIRONMENT

3.1 Natural Sources

Fluorine is the thirteenth most abundant element making up approximately 0.06 to 0.09% of the Earth's crust (Environment Canada 1976; Smith 1983). In nature, fluorine is widely found in sedimentary phosphate rock deposits and minerals (Kirk-Othmer 1980). Total fluorine reserves in phosphate rock with low fluorine content (*i.e.*, 3 - 4%) are estimated at 789 X 10^6 tonnes (Kirk-Othmer 1980). The main fluorine containing minerals are calcium fluoride, fluoroapatite and cryolite. For industrial purposes, the most important source of fluorine is the mineral calcium fluoride (fluorite or fluorspar; CaF_2) with a fluorine content of 49% (Fuge 1988; Government of Canada 1993; Greenwood and Earnshaw 1984). Fluorite, commercially known as fluorspar, occurs as a vein-mineral and is usually associated with quartz, calcite, dolomite or barite (Prud'homme 1990). Although the largest amount of fluoride exists in the form of fluoroapatite [$Ca_5(OH,F)\cdot(PO4)_3$], this mineral is mined mainly for its phosphate content because of its low content of inorganic fluorides (4% fluorine) (Kirk-Othmer 1980; Ney 1979). Cryolite (Na_3AlF_6) (54% fluorine) is rare, and found only in Greenland.

In addition to calcium fluoride, fluoroapatite and cryolite, a number of other silicates, oxides, carbonates, sulphates and phosphates such as topaz (Al_2SiO_4 $(OH,F)_2$), sellaite (MgF_2) and sodium fluoride or villiaumite (NaF) contain minor amounts of inorganic fluorides (Table 3) (Fuge 1988). Also, host minerals such as micas (layer silicates), amphiboles (chain silicates), apatite and tourmaline (Na, Ca)X_3 (Al, Fe^{3+})$_6$ (OH, F) $(BO_3)_3\cdot Si_6O_{18}$, where X is Li and Al, or Mg^{2+}, or Fe^{2+}, or Mn^{2+}, and clays like montmorillonite, kaolinite, and bentonite contain inorganic fluorides (Reimann and de Caritat 1998).

Fluorine and chlorine occupy the hydroxyl sites of hydroxysilicates such as micas, amphiboles and apatite, and the fluorine content of these minerals is particularly high when they occur in granitic rocks (Fuge 1988). In sedimentary rocks, fluorine occurs in the hydroxy minerals including the clays. Inorganic fluoride minerals are more stable than those containing chlorine because the ionic radius is the same as that for the hydroxyl ion, thus minimising lattice distortion.

Inorganic fluorides are released naturally into the environment through the weathering of minerals, emissions from volcanoes, and as marine aerosols (Government of Canada 1993). The most important natural source of inorganic fluorides in the environment is bedrock, from which inorganic fluoride-containing minerals are leached by groundwater, and thence into surface and sea water. Another major natural source of inorganic fluorides is volcanoes which release gases and ash into the atmosphere either by explosive eruptions or by continual low energy release (Kawaratani and Fujita 1990). Estimates of annual global releases of gaseous fluoride compounds (primarily HF) from volcanic sources (passive degassing and eruptions) range from 60 000 to 6 000 000 tonnes, 10% of which are injected directly into the stratosphere (Symonds et al. 1988; Environment Canada and Health Canada 1996). Kawaratani and Fujita (1990) measured mean levels of various chemical species in precipitation around the Sakurajima volcano in Japan and found there was a significant increase in levels of inorganic fluorides in the vicinity of the volcano. In the case of volcanoes with a volcanic eruption index of four or greater, significant amounts (5 000 to 50 000 tonnes) of HF are deposited directly into the stratosphere (Symonds et al. 1988). At present, the

consequences of increased stratospheric levels of the fluoride ion are not known. Estimated emissions of sulphur dioxide, chloride, and fluoride from volcanoes are summarised in Table 4. Finally, about 0.02 X 10^6 tonnes of inorganic fluorides may be released annually from marine aerosols (*i.e.*, mixture between water and gas) (Symonds et al. 1988).

Table 4. Estimated Global Emissions of Inorganic Fluorides from Volcanoes and Industry

Source	SO_2 (10^6tonnes/a)	HCL (10^6tonnes/a)	HF (10^6tonnes/a)
Total Volcanic Emission	18.7	0.4-11	0.06-6
Degassed into Troposphere	17.0	0.3-10	0.05-5
Erupted into Stratosphere	1.66	0.1-1	0.0005-0.5
Sea Salt from Oceans	-	300	0.02

Source: Symonds et al. (1988)

3.2 Anthropogenic Sources

In Canada, the primary anthropogenic emission sources of inorganic fluorides are phosphate fertiliser production (34.6%), and aluminium smelting operations (35.2%) (Environment Canada 1993; Environment Canada and Health Canada 1996; P. Paine 2000, Environment Canada, pers. com.). Other important emission sources include coal burning facilities, oil refining, steel production, chemical producers, primary copper and nickel production, clay production, magnesium smelting, lead and zinc smelting, glass and enamel making, brick and ceramic manufacturing, production of glues and adhesives, fluoridation of drinking water, fluoride-containing pesticides, waste from sewage sludge, and the production of uranium trifluoride (UF_3) and uranium hexafluoride (UF_6) for the nuclear electric industry (Table 5) (Burns and Allcroft 1964; Neumüller 1981; Fuge 1988; Fuge and Andrews 1988; Government of Canada 1993).

Table 5. Estimated Anthropogenic Inorganic Fluoride Releases into the Canadian Environment

Sector	Coverage[a]	Annual Releases (tonnes)			
		Air	Water	Land	Total[b]
Chemical producers	5/7	2	32	177	211 (1.7%)
Clay products[c]	3/9	25	NR	NR	25 (0.2%)
Coal-burning utilities	3/4	543	555	NR	1 098 (8.8%)
Magnesium producers[d]	1/1	100	NR	NR	100 (0.9%)
Oil refining	3/3	24	100	784	908 (7.2%)
Phosphate fertiliser producers	5/6	54	4 169	75	4 298 (34.6%)
Primary aluminium producers	5/5	4 063	307	NR	4 370 (35.2%)
Primary copper and nickel producers	2/3	27	4	186	217 (1.7%)
Steel producers	6/12	239	254	430	923 (7.4%)
Other[e] (Smelter Pb/Zn)	1/2	148	133	2	283 (2.3%)
Total	34/52	5 225 (42%)	5 554 (44.7%)	1 654 (13.3%)	12 433

Source: Environment Canada (1993); P. Paine 2000, Environment Canada, pers. com.
NR = not reported
Notes:
[a]Number of reporting facilities versus number of facilities surveyed
[b]Number in parenthesis refers to percent of total inorganic fluorides released by sector
[c]Values appear low compared to estimates from the U.S. for the same sector
[d]Released as SF_6
[e]Includes motor vehicle manufacturing, glue and adhesive production

As only 65% of the facilities surveyed actually reported releases, estimates presented in Table 5 may be underestimated, particularly for the steel producers and clay products sectors (Government of Canada 1993). Nevertheless, the total estimated annual release of inorganic fluorides from anthropogenic sources to the Canadian environment (air, land, and water) is in excess of 12 400 tonnes/a (Government of Canada 1993; P. Paine 2000, Environment Canada, pers. com.). Atmospheric emissions account for at least 5 200 tonnes (42%) of inorganic fluorides released (predominately as inorganic fluorides), while over 5 500 tonnes (44.7%) are discharged to waters. Releases of inorganic fluorides to land are estimated to exceed 1 600 tonnes (13.3%) (Table 5). Aluminium smelting (4 370 tonnes; 77% of all reported releases to air), phosphate fertiliser production (4 298 tonnes; 75 % of all reported releases to water), are the known major sources of inorganic fluoride releases to air, water, and land (Government of Canada 1993; Environment Canada and Health Canada 1996; P. Paine 2000, Environment Canada, pers. com.). Collectively, these sources account for over 70 % (~8 700 tonnes) of the total release of inorganic fluorides to the Canadian environment.

Table 6 provides information on primary anthropogenic sources, specifically Canadian Aluminium Producers, in Canada.

Table 6. Primary Canadian Aluminium Producers in 1992

Producers	Plants	Production Capacity (tonnes Al)
Alcan Smelters and Chemicals Ltd.	Kitimat, BC	272 000
	Arvida, Jonquière, QC	232 000
	Laterrière, QC	204 000
	Grande-Baie, QC	180 000
	Shawinigan, QC	84 000
	Isle-Maligne, Alma, QC	73 000
	Beauharnois, QC	48 000
Aluminerie Alouette Inc.	Sept-Iles, QC	215 000
Aluminerie de Bécancour Inc.	Bécancour, QC	360 000
Aluminerie Lauralco Inc.	Deschambault, QC	215 000
Canadian Reynolds Metals Company Ltd.	Baie-Comeau, QC	400 000
Total		2 283 000

Source: Environment Canada and Health Canada (1996)

Fertiliser Production

The phosphate fertiliser industry generally produces phosphoric acid, normal superphosphate, triple superphosphate, ammonium phosphate and sulphuric acid; each chemical is characterised by different types and levels of emission. The production of phosphoric acid and superphosphate produce the largest amounts of inorganic fluorides. In the manufacture of superphosphate, the rock is ground, mixed to form a slurry and then sent to a pug mill where very rapid, highly exothermic mixing takes place. From here, the slurry moves along a slow conveyor while mixing continues. Approximately 95% of the inorganic fluoride emissions occur in the conveyor belt area. The inorganic fluorides in the gas stream are scrubbed with water or dilute fluorosilicic acid, before the water is discharged to a water-containment system and reused. For normal superphosphate, 10 and 50% of the inorganic fluorides in the phosphate rock is released to the environment, while for triple superphosphate the quantity ranges from 32 to 45% (McBeath 1987).

In Trail, BC, a fertiliser plant produces phosphate from the reaction of sulphuric acid with phosphate rock. This process releases large quantities of particulates and gaseous inorganic fluorides. The gas is captured in the wet scrubber system and used in the manufacture of fluorosilicic acid, which in turn is used as an electrolyte in lead refineries, or sold as a fluoridating agent for domestic drinking water supplies (White et al. 1986). Prior to 1986, the major source of particulate inorganic fluoride emissions was the fertiliser complex while the major source of gaseous inorganic fluoride emissions was the lead refinery. Since this time, a scrubber system has been installed in the refinery resulting in decreases in airborne inorganic fluorides in the vicinity of the plant (White et al. 1986).

Kabata-Pendias and Pendias (1984) found that phosphate fertilisers contain up to 38 mg F⁻/kg resulting in an estimated accumulation of an additional 89 mg F⁻/kg soil over a 10 year period. According to another estimate, the average inorganic fluoride content of superphosphate fertiliser used in Tasmania is 1.35%, from which it was calculated that on average, 2.02 kg inorganic fluorides are applied per hectare per year (Mason et al. 1989). In Germany, fertiliser application contributes between 3 and 8 kg F⁻/acre, while additions to the soil from atmospheric deposition is between 2.77 and 8.73 kg F⁻/acre (Oelschläger 1971). In the U.S., 5 million tonnes of phosphate fertiliser was applied to the soil in 1973. Assuming the inorganic fluoride content is 2%, then 100 000 tonnes of inorganic fluorides were added to the soil that year (Chemical and Engineering News 1974).

Aluminium Smelting

Primary Aluminium Production contributes over 75% of the total HF air emissions in Canada (Table 5). Aluminium producers in Canada (1 in Kitimat, British Columbia, and 10 in Quebec) are the main anthropogenic sources of HF air emissions (Table 6). Specific to aluminium production, most of the primary losses of inorganic fluorides or fluoridated emissions come from the smelting production process. Since molten cryolite is utilised as a bath for the electrolysis of alumina, the fume emitted from the electrolytic cell contains gaseous inorganic fluorides (mainly hydrogen fluoride) and particulate inorganic fluorides. Gaseous inorganic fluorides are contained also in the exhaust gas of the anode baking furnace, arising from the recycling of anode butts. The amount of inorganic fluorides emitted depends on the cleanliness of the butts, where unscrubbed emissions contribute substantially to the overall releases from the smelter. Small amounts of inorganic fluorides are emitted also from cast-house furnaces when the metal or alloys are treated by fluxes containing inorganic fluorides (UNEP 1986).

A number of estimates of other aluminium related emissions for inorganic fluorides have also been made, some of which are summarised in Table 7; however, there is a great deal of uncertainty associated with these estimates, as exemplified by recent data on aluminium smelter emissions. Emission factors for total inorganic fluorides were 1.0 tonne F/tonne Al for the Söderberg pots and 0.43 tonne F/tonne Al for the prebake pots (Houle et al. 1991). Stricter legislation, upgrading the manufacturing equipment and improvements to the control technology decrease inorganic fluoride emissions. For example, in 1981, 9 711 tonnes of potlining were deposited in an aluminium production landfill, before passing though two settling ponds and discharged into the Kitimat Arm, BC. The mean inorganic fluoride level of the leachate for 1980-1981 was 523 mg F⁻/L (Warrington 1987).

Table 7 shows industrial emission types for fluoride-containing substances. Although no values are given, the table illustrates whether emissions are gaseous, particulate or introduced directly into water as effluent.

Table 7. Emission Types for Various Industries

Industry	Emission Type	Speciation[a,b]	Emission Source	Reference
Elementary Phosphorus				
	Gaseous	HF, SiF_4	Pellet plant, grate-kiln-cooler section	Roberts and Thompson (1980)
	Particulate	NR	Pellet & furnace plant stacks, handling of raw material, waste, and slag	
	Effluents	NR	Wet gas scrubbers.	
Aluminium Smelting				
	Gaseous	HF, CF_4, C_2F_6, SiF_4	SiF_4 and AlF_3 reaction in water vapour, and hydrogen-inorganic fluorides reaction in carbon anode.	Low and Bloom (1988)
	Particulate	Na_3AlF_6, $Na_5Al_3F_{14}$, CaF_2, AlF_3, NaF	All are used or formed in smelting[c]	
	Effluents	CaF_2, MgF_2, AlF_3, NaF	Wastewater from wet scrubbers; may be present in settling pond leachate	Pickering et al. (1988)
	Leachate	Various F compounds	Solid waste disposal sites	
Phosphate Fertiliser				
	Effluent	HF, SiF_4	Acidification of ore[d], mixing, denning, curing, storing[e]	McBeath (1987)
		H_2SiF_6, SiF_4	Acidification of ore	
	Gaseous	HF, SiF_4	Denning, curing[f]	
	Acid sludge	"fluosilicates", and "inorganic fluorides"[g]	Phosphoric acid clarifier	

Source: Environment Canada (1994)
NR = not reported
Notes:
[a]Hydrogen fluoride (HF), silicon tetra fluorides(SiF_4), carbon tetrainorganic fluorides (CF_4), hexafluoroethane (C_2F_6),cryolite (Na_3AlF_6), chiolite ($Na_5Al_3F_{14}$), calcium fluoride (CaF_2), aluminium inorganic fluorides (AlF_3), fluorosilicic acid (H_2SiF_6)
[b]Data on speciation of inorganic fluorides in particulate and effluent emissions was not located
[c]Two particulate fractions exist: 1) coarse particulates, approximately 20 µm in diameter with 10-20% F, existing as agglomerates or absorbed on entrained carbon or alumina, and 2) fine particulates, <0.5 µm, with 20-30% F, existing as sublimated vapour from the pots
[d]HF and SiF_4 can be produced by the following reactions:

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$
$CaF_2 + 2H_3PO_4 \longrightarrow Ca(H_2PO_4)_2 + 2HF$ (HF reacts with Si in rock)
$6HF + SiO_2 \longrightarrow H_2SiF_6 + 2H_2O$ (may dissociate, $H_2SiF_6 SiF_4 + 2HF$)

[e]Emissions (*e.g.*, mainly SiF_4) occur during manufacture of normal and triple superphosphate fertilisers
[f]In the manufacture of normal and triple superphosphate, volatilisation of SiF_4 can also occur prior to reaction with water
[g]Products arise from impurities in the minerals that settle out in the clarifier

Inorganic fluoride emissions from an aluminium smelter in Tasmania in 1984 include: 5.22 kg/tonne from scrubbers; 2.72 kg/tonne from roof louvers; and 0.35 kg/tonne from the carbon baking plant (Low and Bloom 1988). Low and Bloom (1988) also presented data on wet and dry deposition in the vicinity of the Tasmanian aluminium smelter, and examined various fluorine-containing compounds that may be emitted during smelting operations. Volatile compounds are hydrogen fluoride (HF), carbon tetrafluoride (CF_4), hexafluoroethane (C_2F_6) and silicon tetrafluoride (SiF_4), while among the particulates (either a coarse fraction with an average particle diameter of 20 mm or a fine fraction of submicron size) are cryolite (Na_3AlF_6), chiolite ($Na_5Al_3F_{14}$), calcium fluoride (CaF_2), aluminium fluoride (AlF_3) and sodium fluoride (NaF). Coarser particulate fractions

consist of agglomerates that contain 10-20% by weight of F^-, while the finer fractions are derived from the pots with an average F^- content of 20-30% by weight. Approximately 35-44% by weight of the uncontrolled emissions are submicron particles which are difficult to remove from the gaseous effluents. Low and Bloom (1988) reported annual mean deposition rates ranging from a "background" level of about 90 g $F^-/m^2/d$ to 12 568 g $F^-/m^2/d$ within 1 km of the smelter. Wet deposition predominated during autumn and winter.

The major industrial source of inorganic fluorides is the aluminium smelting industry with other contributions from the elementary phosphorus industry and stainless steel production (Table 8).

Table 8. Emissions for Various Inorganic Fluorides Emitting Industries

Industry	Location	Emission (kg F/tonne)[a]	Emission Factor (kilotonnes/a)	Production Capacity (tonnes F)	Reference
Aluminium Smelter	Baie-Comeau, QC	12.0	614	7368	Conseil Consultatif de l'Environnement (1986)
Aluminium Smelter	Alma, QC	2.7	299	807	
Aluminium Smelter	Jonquière, QC	3.5	1720	6020	
Aluminium Smelter	La Baie, QC	0.41	177	73	
Aluminium Smelter	Shawinigan, QC	4.1	344	1410	
Aluminium Smelter	Melocheville, QC	12.2	188	2294	
Aluminium Smelter	Becancour, QC	0.014[b]	360	3358	Gonthier (1991)
Aluminium Smelter	Beauharnois, QC	0.66[b]	50	3300	Groupe d'Intervention du Plan d'Action Saint- Laurent (1991)
Elementary Phosphorus	Varennes, QC	32.85[b]	25	295 730	Gonthier (1991)
Stainless Steel	Tracy, QC	0.7 (t/d)	60	256	Groupe d'Intervention du Plan d'Action Saint- Laurent (1991)

Source: Environment Canada (1994)

Notes:

[a]Emissions based on calculation of emission factors and annual production

[b]Values calculated are for years 1980-1983, and using (kg F^-/d x 365d/a)/tonnes/a

3.2.1 Water Fluoridation and Treatment

According to available estimates, approximately 40% of the Canadian population receives fluoridated water (OMEE 1997). Sewage effluents from municipalities using fluoridated drinking water discharge significant amounts of inorganic fluorides. Alberta fluoridates approximately 385 million m^3 of municipal water or sewage water each year. Levels of inorganic fluorides in treated water concentration are regulated at 1.0 ± 0.1 mg/L monthly, and 1.0 ± 0.2 mg/L daily. The concentration of inorganic fluorides in municipal wastewater at 276 locations in Alberta averaged 0.62 mg/L (n = 282), ranging from 0.07 to 4.804 mg/L (Alberta Environment 1992). In the populated centres of Greater Victoria and Greater Vancouver, British Columbia, fluoridated water is not used, but twenty-two smaller communities (total population about 321 000) add inorganic fluorides in the form of NaF, Na_2SiF_6 or H_2SiF_6 to their water supply (Gunther and Gray 1988, pers. com.). In Ontario, some water treatment plants fluoridate. A conventional water treatment plant in Ajax, ON, serves a population of 105 000 by fluoridating water (55×10^3 m^3/d) from Lake Ontario. Another plant located in Belleville, Ontario, fluoridates water from the Bay of Quinte (54.6×10^3 m^3/d) for a population of 36 800 (OMEE 1997). Groth (1975b) estimated that fluoridation of drinking water in the U.S. releases approximately 20 000 tonnes of inorganic fluorides (mostly sodium inorganic fluorides) to the aquatic environment for every one hundred million people supplied. Equivalent Canadian estimates are not available.

3.2.2 Other Sources

A report prepared by the Ministry of the Environment of Ontario, noted that the effluents from a pulp and paper mill in Cornwall, ON, were a major source of inorganic fluoride releases to the St. Lawrence River. The origin of the inorganic fluorides in these effluent samples was not identified (Kauss et al. 1989). Switch gear insulation gas and magnesium smelting are known major uses of sulphur hexafluoride (SF_6) in Canada. These industries are believed to be virtually non-destructive and ultimately dispersive, with total annual releases to the Canadian environment expected to be at least equal to 110 tonnes of SF_6. Canada contributes approximately 1-3% of the annual global atmospheric release of 5 000 to 8 000 tonnes SF_6 (based on 1990 data, Environment Canada 1993).

High atmospheric levels of inorganic fluorides have been observed in the vicinity of certain brickworks in England where high levels of fluorosis in farm animals have been observed (Fuge and Andrews 1988). Other studies on brickworks in Belgium have shown significant emissions of hydrogen fluoride and silicon tetrafluoride which are liberated during the firing process (Debackere and Delbeke 1978). Between 30 and 95% of the inorganic fluorides present in the clay (muscovite and illite) are released during processing. Furthermore, if coal is used in the firing ovens, approximately half of its inorganic fluoride content will be emitted. Horner (1989) measured the atmospheric levels of inorganic fluorides in the vicinity of a glass works in Rothanham, England. Samples taken at a distance of approximately 300 m from the factory showed that gaseous inorganic fluoride levels ranged from 1 to 6 g F^-/m^3 while particulate fluorine levels ranged from 0 to 1 g F^-/m^3. Background levels of inorganic fluorides for this region were <0.1 g F^-/m^3. The author reported that prior to the installation of controls at the factory, hydrogen fluoride emissions caused etching of windows in local buildings. For this study, soil, vegetation and gutter dust levels were measured and all three

parameters were found to be significantly higher closer to the factory compared to a location 500 metres from the factory.

3.3 Waste Management

Industrial wastes contain inorganic fluorides of generally three types: stack gases, liquid effluents and solid waste. Table 9 illustrates some commonly applied methods for waste treatment methods for removing inorganic fluorides from municipal and industrial effluents. For a complete discussion of waste control/reduction technologies, refer to McBeath 1987; Patterson 1985; UNEP 1986; Slooff et al. 1989; Lavalin Environnement 1990a;b.

Davison et al. (1973) reported high levels (0.0003 mg F^-/m^3) of atmospheric inorganic fluorides nearby burning coal mine waste heaps. Mean estimate of the inorganic fluoride content of coal used in a coal-fired power plant in Hunter Valley, Australia, is 234 F^-mg/g coal (range 97 - 425 mg F^-/g). The coal consumption of this particular plant is normally about 4.8 Mt/a (Murray 1984a). A substantial amount of inorganic fluorides could be emitted assuming that half the inorganic fluoride content of the coal is emitted as gaseous and particulate emissions. Some granite rocks, such as the area of St. Austell granite in Cornwall, England, have undergone intense kaolinisation (formation of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_20$ from feldspar and other minerals) (Neumüller 1983) for use in the china-clay industry. The waste-tips from these china-clay workings are inorganic fluoride-rich, and as much of the waste has a fine grain size, it is easily dispersed and constitutes a significant source of contamination (Fuge and Andrews 1988). Other waste such as mine tailings with a high fluorite content may be a significant source of contamination, as contaminant levels in the run-off and vegetation surrounding these tailings may also contain elevated levels of inorganic fluorides (Fuge and Andrews 1988). Also, on one UK farm the application of sewage sludge as fertiliser was associated with an outbreak of fluorosis in cattle (Davis 1980). It is suggested that sewage sludge from industrial areas with high inorganic fluoride levels should not be used for agricultural purposes because of possible contamination (Fuge and Andrews 1988).

Table 9. Summary of Selected Treatment Methods for Removal of Inorganic Fluorides from Industrial/ Municipal Effluents

Treatment Process	Inorganic fluorides concentration (mg/L)		Current Application
	Initial	Final	
Lime	45-3000	6-40	Industrial
Lime + 16 hour settling	200-700	8	Industrial
Lime, 2 Stage Process	1460	9	Industrial
Lime + Calcium Chloride		12	Industrial
Lime + Calcium Carbonate, 2 Stage Process	11 100	6	Industrial
Lime + Alum	2020	2.4	Industrial, Pilot Study
Alum	3.6	0.6-1.5	Municipal
Alum	60	2	Industrial, Lab Scale
Hydroxyapatite Beds, Synthetic	10-13	0.5-1.6	Municipal
Hydroxyapatite Beds, Bone Char	6.5-12	0.6-1.5	Municipal
Alumina Contact Bed	4.5-8	0.1-1	Municipal
Alumina Contact Bed	9	1.3	Industrial, Lab Scale
Alumina Contact Bed	20-40	2-3	Industrial, Pilot Scale[a]
Granulated Slag Treatment	700	25-30	Industrial[b]

Source: Adapted from data presented in Patterson (1985)
Notes:
[a]This method may not have industrial applications as it has not been shown to be capable of removing >95% of the pollutant (McBeath 1987)
[b]Process described by McBeath (1987) for the treatment of phosphate fertiliser plant wastewater effluents

3.4 Production and Uses

Production

At present, there are no fluorspar mines operating in Canada. A plant located in St. Lawrence, NF, processes, and until 1990 mined acid grade fluorspar. In 1989, the reserves available were estimated to be 5 million tonnes and production averaged 200 tonnes per day (Prud'homme 1990). The majority of the acid grade fluorspar produced at this plant was exported to the United States. Currently, Canadian chemical manufacturers import acid grade fluorspar from countries such as Mexico and the United States for the production of hydrofluoric acid. In 1988, imports of fluorspar were approximately 195 057 000 tonnes and in the first nine months of 1989, imports totalled 92 398 tonnes (Prud'homme 1990).

The leading producer of hydrogen fluoride (HF) in Canada, located in Amherstburg, ON, manufactured 56 000 tonnes HF in 1992. The other main producer, located in Jonquière, QC, manufactured 28 000 tonnes HF in 1992 (CIS 1996). Together these plants produce about 2/3 of the total HF in North America. The aluminium smelting industry operates one aluminium fluoride plant in Canada, which, at full capacity can produce 45 000 tonnes AlF_3 per year. The company imported 60 000 tonnes of fluorspar from Morocco and China (Prud'homme 1990).

Phosphate fertilisers are produced at seven plants in Canada; one in New Brunswick, one in Manitoba, three in Alberta, and two in British Columbia. Phosphate rock, most commonly fluoroapatite, forms the raw material for production. The seven plants generally produce five products: phosphoric acid, normal superphosphate, triple superphosphate (less frequently produced), ammonium phosphate and sulphuric acid. In 1996, 1.14 million tonnes of phosphate bearing rock was imported to Canada (P. Lansbergen 1999, Canadian Fertiliser Institute, pers. com.). About 175 000 tonnes of P fertiliser were produced in 1996 in Canada (FAO 1999). Of this, 7 900 tonnes were exported. An additional 129 000 tonnes were imported. More recent information suggests these values may have decreased due to plant closures (P. Paine 2000, Environment Canada, pers. com.)

Uses

The aluminium manufacturing industry uses approximately 15 to 30 % of the hydrofluoric acid consumed in Canada. In 1988, the industry also consumed 35 825 tonnes of aluminium fluoride (AlF_3). Quebec smelters used a combination of sources of AlF_3, while British Columbia smelters relied entirely on foreign sources from Norway and Japan (Prud'homme 1990). Hydrofluoric acid is used in the manufacture of AlF_3 and cryolite, both of which are used in the aluminium industry. The production of 1 tonne of aluminium consumes on average 23.7 kg of AlF_3. In older smelters, the amount is approximately 30 kg/tonne, while in modern smelters, approximately 15 kg/tonne are used (Prud'homme 1990). AlF_3 is used to lower the melting point of the electrolyte in the aluminium refining process (Prud'homme 1990). A typical electrolyte mixture used in aluminium smelters consists of 80-85% Na_3AlF_6, 5-7% AlF_3 and 5-7% CaF_2. Synthetic cryolite is used as a flux in the electrolytic reduction of Al_2O_3 to aluminium by the Hall-Héroult process. Synthetic cryolite may be manufactured due to shortages of cryolite, by treating aluminium hydroxide with hydrogen fluoride under alkaline conditions:

$$6HF + Al(OH)_3 + 3NaOH \longrightarrow Na_3AlF_6 + 6H_2O$$

Consumption of fluorspar in Canada peaked at 180 000 tonnes in 1988 and 1989, declined to 14 978 tonnes in 1994, but has been on the rise since. The most recent report is 92 822 tonnes in 1998 (Energy, Mines and Resources Canada 1989; Natural Resources Canada 1995; 2001). Fluorspar is used in the manufacture of HF, metallurgical processes and ceramic wares. In the glass manufacturing industry, fluorspar and sulphuric acid are heated in rotary kilns. The resulting gas is condensed to form hydrofluoric acid. This acid is used for etching and polishing glass and silicon chips and in dilute solution for cleaning stonework (Horner 1989). Metallurgical grade fluorspar is used to remove impurities during melting and increase the fluidity of slag in the furnace during the manufacture of steel (Prud'homme 1990).

Other substances manufactured include uranium tetrafluoride (UF_4) and uranium hexafluoride (UF_6), both of which are used in uranium refining. UF_6 is volatile, and the gaseous uranium compound is separated by a diffusion process. Nuclear fuel is produced from UF_6 at a plant in Port Hope, ON. UF_6 can be released into the atmosphere unintentionally, producing HF and uranyl fluoride (UO_2F_2). Models of transport for UF_6 have been discussed by Nair et al. (1998).

HF is used in the production of motor gasoline alkylates and inorganic fluoride salts, ceramics, steel pickling and glass etching (CIS 1991). HF is used in the polishing of television picture tube screens and funnels and to frost incandescent lamp bulb envelopes (Patterson 1985). HF has been used also in the manufacture of CFCs, although the demand for these chemicals (which are used as refrigerants, solvents and blowing agents) is decreasing as a result of the Montreal Protocol in September 1987. In 1987-1988, the quantity of CFCs used in Canada was in the order of 23 000 tonnes (Prud'homme 1990). Finally, HF is utilised in electroplating and as a catalyst at several stages in the oil-refining process (Prud'homme 1990). The Canadian demand for HF used in the production of products and export sales was forecast to increase by 1998 (Table 10). More current data is not available.

Table 10. Canadian Demand for Hydrogen Fluoride

Substance	Demand (tonnes per annum)			
	1993	1994	1995[a]	1998[b]
Aluminium fluoride	31 400	31 500	30 000	33 100
Export Sales	100	100	100	15 000
Fluorochloromethanes	900	1 000	800	1 400
Miscellaneous (including motor gasoline alkylate)	1 500	1 700	2 600	2 200
Total Domestic Demand	37 100	38 500	37 300	41 200
Uranium hexafluoride	3 300	4 300	3 900	4 500
Total	74 300	77 100	74 700	97 400

Source: CIS (1996)
Notes:
[a]Estimated demand
[b]Forecasted demand

4. ENVIRONMENTAL FATE

As discussed, inorganic fluorides are introduced into the environment as a result of natural emissions (*e.g.*, volcanic activities) or anthropogenic sources. Depending on meteorological conditions and season, gaseous and particulate inorganic fluorides are transported in the air and ultimately, are deposited as either wet or dry deposition on land or open water bodies. Inorganic fluorides in soil are bound in bentonite, kaolinite or montmorillonite clays as substitutes for OH^- ions and eventually, leached into groundwater. In the presence of Al^{3+} and Ca^{2+} ions, complexation may take place depending on the pH of the water or soil. Inorganic fluorides in surface water are taken up by aquatic and terrestrial biota or plants.

The fate of inorganic fluorides in the atmosphere is influenced primarily by vaporisation, aerosol formation, wet/dry deposition, and hydrolysis. In water, mobility and transport of inorganic fluorides are dependent on pH, water hardness, and the presence of ion-exchange minerals, containing calcium and aluminium (*e.g.*, clays), as well as the content of silicic acid. The mobility of inorganic fluorides in soil is affected by the fluoride concentration, alkalinity, pH, soil type, complexation with aluminium and calcium, and presence of organic matter, and selenium ions as either SeO_3^{2-} (selenite) or SeO_4^{2-} (selenate). Fate of inorganic fluorides in biota is mainly determined by route of exposure, levels of bioavailable inorganic fluorides, and uptake/excretion kinetics. Although quantitative estimates of amount, residence times, and kinetics of inorganic fluorides have not been completely delineated in different media, a number of estimates have been made for background and anthropogenic levels.

Terrestrial plants take up inorganic fluorides directly from air by their leaves or indirectly from rain or groundwater by their roots. Airborne inorganic fluorides are probably the most important source of inorganic fluorides for plants. Levels of inorganic fluorides in rainwater appear to be positively correlated with levels in plants (Kabata-Pendias and Pendias 1984). Animals take up inorganic fluorides by feeding on these plants or drinking water. Murray (1981) suggests a possible cycling from soils to vegetation and from vegetation to wildlife. Animal death and plant decomposition return fluorides to the soil and ultimately, to groundwater. In surface waters, inorganic fluorides are taken up by plants, and aquatic, semi-aquatic, and terrestrial biota. Eventually, inorganic fluorides are recycled in the water (*e.g.*, decomposition), and may be incorporated in apatite, bentonite clays, or precipitate as CaF_2 (NAS 1971). Although inorganic fluorides deposition, levels and emissions have been studied extensively, only a few experimental studies have been conducted that correlate deposition rates with uptake and vegetation losses.

4.1 Atmospheric Processes

Hydrogen fluoride and other inorganic fluoride particulates (*e.g.*, CaF_2) account for approximately 75 and 25% of global atmospheric inorganic fluoride species, respectively. The gaseous emissions consist mostly of HF, silicium tetrafluoride (SiF_4), fluorine (F_2), hydrofluorosilicic acid (H_2SiF_6), and SF_6. As particulates Na_3AlF_6, AlF_3, CaF_2, sodium fluosilicate (Na_2SiF_6), lead fluoride (PbF_2), and $Ca_5(F,OH)\cdot(PO_4)_3$ are also present (Health Council of the Netherlands 1990). Inorganic fluorides combine with water vapour to produce an aerosol or fog of aqueous hydrofluoric acid. Some fluoride-containing compounds remain in the atmosphere for a long time, for example, the

estimated residence time of SF_6 ranges from 500 to several thousand years (Ramanathan et al. 1985; Chu 1991).

Non-volatile inorganic fluoride particulates are removed from the atmosphere via condensation or nucleation processes. Most inorganic fluoride particulates emitted into the atmosphere are stable (CPHA 1979). Given their low to moderate water solubility, particulates are usually deposited by dry deposition, whereas gaseous species are mainly deposited by wet deposition (Murray 1981). In the case of wet deposition of gaseous inorganic fluorides, a high water potential at the soil surface and high relative humidity promote the formation of dilute acid droplets which may increase deposition (Murray 1981). Wet deposition, and incorporation of atmospheric inorganic fluorides into precipitation can occur either in-cloud or below-cloud. In the cloud, 'rainout' occurs by condensation of water vapour on aerosol particles, particularly those that are water-soluble or hygroscopic. Falling raindrops and snowflakes can also capture aerosol particles due to their different sedimentation velocities (*i.e.*, washout) (Rohbock 1982). The relative contributions of 'rainout' and washout cannot be determined from analysis of precipitation.

Meteorological conditions, especially wind speed and direction, particle size, seasonal climatic conditions and topography (*e.g.*, sampling locations) have the strongest influence on the distribution of atmospheric inorganic fluorides (Low and Bloom 1988; Thane 1988). Although few data exist on the deposition of inorganic fluoride-containing particulates, the influence of the particle size and washout factor is discussed in general by Rohbock (1982). Low and Bloom (1988) monitored wet and dry deposition of inorganic fluorides in the vicinity of a Tasmanian aluminium smelter. The researchers hypothesised that wet deposition dominates during winter (high rainfall) and dry deposition dominates during summer (low rainfall). Low and Bloom (1988) reported that soluble F^- levels vary from 0.09 to 12.5 $mg/m^2/d$ about 1 km southeast of the emission source, with the highest levels occurring within 3 km of the emission source. The deposition of soluble F^- may be affected more by rainfall than other trace elements such as Al or Mn (Low and Bloom 1988). Gaseous and submicron particulate inorganic fluorides were carried up to 10 km from the emission source by prevailing winds. The highest deposition rate for soluble F^- occurred in autumn, corresponding to the season of highest precipitation; however, the period with the lowest precipitation (*i.e.*, summer) did not have the lowest deposition rate. Wet deposition was the predominant method of inorganic fluorides removal in winter while dry deposition was more significant during summer. Hocking et al. (1980) reported similar results in their studies of ambient air inorganic fluoride levels near the Kitimat, BC, aluminium smelter for the years 1975-1979. The authors found that dry deposition of inorganic fluorides was quantitatively more important during the dry season than wet deposition. The main factors influencing ambient inorganic fluoride levels were operating conditions at the plant (mechanical and human error) and wind speed and direction.

In a similar study, Kotturi (1990) examined the effect of HF on the pH of precipitation by measuring the inorganic fluoride content of specific precipitation events near the aluminium smelter at Kitimat, BC. Emission sources of HF were tracked using a trajectory analysis on the air parcel. The results showed that ambient air levels of inorganic fluorides decreased with increasing precipitation and that levels of inorganic fluoride were highest in summer when rainfall was lower. These findings corroborate those comparable studies by Low and Bloom (1988) and Hocking et al. (1980).

Although the general nature of inorganic fluoride deposition is well described in the literature, the exact behaviour of various inorganic fluoride species in the atmosphere is complex (Thane 1988). This author attempted to correlate emissions of inorganic fluorides from a Norwegian aluminium smelter with inorganic fluoride levels at monitoring stations at varying distances, taking into consideration weather patterns. Because the smelter was the major emitter of inorganic fluorides in the region, a significant correlation between emission and monitoring data was expected, but was not observed. Thane (1988) suggested that this lack of correlation could be accounted for if: 1) inorganic fluorides have a long residence time in air, allowing for dispersion by varying wind directions, and 2) inorganic fluorides which are absorbed by soil or vegetation are re-emitted into air.

Kudo et al. (1987) examined the dispersion of inorganic fluorides emitted from aluminium smelters located in the Maurienne Valley in the French Alps. Inorganic fluoride concentrations in both water and sediments showed a consistent, steady increase along four rivers where aluminium smelters were located, with levels being significantly higher further downstream of the aluminium plants. There was, however, no location which showed a particularly high level. This finding suggests that inorganic fluorides are emitted into the air as gases and atmospheric particulates, and subsequently deposited (by rain and snow) into the river, water and sediment. Kudo et al. (1987) estimated net transport rates of inorganic fluorides in rivers of the Maurienne Valley in the French Alps, Europe, to be 665 tonnes/a (97.8%), whereas the net transport rate of inorganic fluorides in bottom sediments was 15 tonnes/a (2.2%). The annual emission rate of inorganic fluorides in the valley was 500 tonnes/a. Overall a gradual decrease in inorganic fluoride load is observed because the amount flowing out via rivers (680 tonnes/a) is greater than the amount produced by aluminium smelter emissions (500 tonnes/a). In general, the major form of dispersion of inorganic fluorides is through wet deposition (rain and snow), which is significantly different from other inorganic fluoride emitting industries, (*e.g.*, fertiliser manufacturing), where inorganic fluorides may be discharged directly into waterways.

Sidhu (1982) monitored deposition of inorganic fluorides in soil humus though precipitation and leaf litter predicting an average deposition of 2 610 mg F^-ha/mm of rain and 3 100 mg F^-/ha/mm of snow water at a site 1.4 km from a major inorganic fluoride emission source (*i.e.*, phosphorous plant) in Long Harbour, NF. Based on deposition rates and precipitation estimates (1 200 mm/a), 3 430 mg F^-/ha/a was deposited closer to the point source while in areas further away, the rate of deposition was <150 mg F^-/ha/a. This level was 5 to 15 times higher than deposition from leaf litter. Accumulation of inorganic fluorides by soil ranged from 7 010 to 10 mg F^-/ha/a at 1.4 km and at 18.7 km from the source, respectively.

In nature, there are typical and constant ratios between specific stable isotopes of elements. A change in this ratio indicates an increase or decrease of one of two isotopes. In a deforested moorland catchment in mid-Wales, the fluoride to chloride ratios (F:Cl) of rain water, throughfall, and stemflow were two orders of magnitude higher than in sea water, suggesting that some enrichment of anthropogenic inorganic fluorides occurs in the atmosphere (Neal et al. 1990). These F:Cl ratios are similar to those seen in areas further from point-sources, indicating that the contribution from atmospheric input was minimal at this location. Levels of inorganic fluorides are higher in throughfall and stemflow than in rain water, showing that rainfall becomes concentrated while passing though the forest canopy, presumably by an evaporative

process. The lower F:Cl ratios in throughfall and stemflow compared with rainfall indicates that the tree canopy must absorb inorganic fluorides from precipitation. In stream water, a seasonal variation occurs, with the highest concentrations occurring in early autumn and the lowest in late winter and early spring. Seasonal variations are accounted for by biological and evapotranspirational factors (Neal et al. 1990). A correlation between the level of inorganic fluorides in rainfall and that in stream water was found, although the F:Cl ratio was higher in the stream than the throughfall. These two observations are not easily explained.

The F:Cl ratios in the environment for rain, throughfall, stemflow, stream water, and sea water in different regions are summarised in Table 11.

Table 11. Measured F:Cl Ratios in Various Environmental Media

Medium (Location)	F:Cl ratio	Reference
Rain (BC)[a]	0.22-2.93	Kotturi (1990)
Rain (NE U.S.)	0.11	Khwaja and Husain (1990)
Rain (Wales)	7.34×10^{-3}	Neal et al. (1990)
Rain (Japan)[b]	0.16	Kawaratani and Fujita (1990)
Throughfall (Wales)	3.85×10^{-3}	Neal et al. (1990)
Stemflow (Wales)	3.72×10^{-3}	Neal et al. (1990)
Stream water (Wales)	$8.2\text{-}8.6 \times 10^{-3}$	Neal et al. (1990)
Sea water	6.7×10^{-5}	Drever (1982)

Source: Environment Canada (1994)
Notes:
[a]Ratios are based on halogen levels at Kitimat and Terrace during storm events in November 1980 and May 1981
[b]Ionic content measured over a 7 month period (1985-86) after the volcanic eruption of Mount Sakurajima. Six locations were monitored at distances of 5-30 km

Although in the past it is generally believed that the sea water-air interface is a major source for the injection of inorganic fluorides into the atmosphere, the data of Barnard and Nordstrom (1982) suggest that precipitation may be a more important source to the atmosphere. These authors found that levels of inorganic fluorides in precipitation in a coastal location (Lewes, DE, U.S.) were lower (mean 0.0056 mg F^-/L) than those in an inland area with no known point-sources (Charlottesville, VA, U.S.) where the mean inorganic fluoride level was 0.010 mg F^-/L. Barnard and Nordstrom (1982) showed also that measured levels of inorganic fluorides in precipitation (mean level 0.0081 mg F^-/L) were close to those predicted from the total input from all sources (0.0116 mg F^-/L). Expected levels of inorganic fluorides in precipitation were calculated for the year 1972 (Table 12).

According to this estimate, at least 2/3 of the inorganic fluorides in precipitation originates from anthropogenic sources (due to wet deposition). Other calculations for the United States showed that approximately 0.020 mg F^-/L result from anthropogenic sources on the eastern seaboard. In contrast, Brimblecombe and Clegg (1988) found that HF from marine aerosols may represent a significant natural source of HF in the troposphere based on calculations of partial pressures of HI and HF over the acidified seasalt aerosols. HF has a substantially greater partial pressure than HCl and is almost

five orders of magnitude less soluble than HCl. They concluded that HF will be preferentially degassed from the aerosol, indicating that the marine aerosol may be totally depleted of inorganic fluorides.

Table 12. Expected Levels of Inorganic Fluorides in Precipitation

Sources of Inorganic Fluorides in Precipitation	Levels of Inorganic Fluorides in Precipitation
Anthropogenic input into atmosphere	3.6×10^{12} mg/a
Global rainfall:	4.8×10^{20} mg/a
From anthropogenic sources	0.0076 mg F^-/L
From dust	0.0010 mg F^-/L
From volcanic activity	0.0030 mg F^-/L
Total	0.0116 mg F^-/L

Source: Barnard and Nordstrom (1982)

4.2 Terrestrial Processes

The most important natural source of inorganic fluorides in soil is weathering of the parent rock (WHO 1984). During weathering, some inorganic fluoride minerals (*e.g.*, Na_3AlF_6) are rapidly broken down, especially under acidic conditions (Fuge and Andrews 1988), while others (*e.g.*, $Ca_5(F,OH)\cdot(PO_4)_3$ and CaF_2) dissolve slowly (Kabata-Pendias and Pendias 1984). The fate and mobility of inorganic fluorides in soil are affected by a number of factors including chemical form, rate of deposition, soil parameters and permeability (Kabata-Pendias and Pendias 1984), pH and buffering capacity (Gilpin and Johnson 1980), presence of calcium (Flühler et al. 1982), iron and aluminium ions (Murray 1983, 1984a;b), selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) (Jinadasa and Dissanayake 1992), organic matter (Flühler et al. 1982; Murray 1983), and moisture content (Davison 1983).

The inorganic fluoride content of soils varies depending on the adsorption ability of the soil to bind inorganic fluorides which is related to the chemistry and proportion of clay, silt and sand components in the soil (Marier and Rose 1971; Gilpin and Johnson 1980; Flühler et al. 1982; Polomski et al. 1982; Davison 1983; Murray 1983; 1984b; Kabata-Pendias and Pendias 1984), whereas the availability of inorganic fluorides to plants is affected by soil adsorption (MacIntire 1950; Garber 1968; Gisiger 1968; Oelschläger 1971; Perel'man 1977; Flühler et al. 1982). Most of the inorganic fluorides in soil are tightly bound, but after years of exposure to anthropogenic inorganic fluorides, the water-extractable inorganic fluoride content in soils may increase significantly (Polomski et al. 1982). Gilpin and Johnson (1980) recorded an increase from 0.005 to 0.01 mg F^-/g/a in Pennsylvanian soils. This rate of increase is comparable to that calculated by Schivela (1979). Assuming that the air level was 1 mg/m^3, Schivela estimated that the deposition rate would be 750 kg F^-/km^2/a, which is the equivalent of 0.011 mg F^-/g on a soil weight basis. However, the actual accumulation in soils is dependent not only on atmospheric input, but also on the rate of translocation though the soil profile (Polomski et al. 1982).

Polomski et al. (1982) studied levels of inorganic fluorides in soils in a forested and grassland region near an aluminium smelter. A systemically different accumulation pattern for water-soluble inorganic fluorides was observed at each location. The soil F^-

concentration in the forest was consistently higher, most notably, the water-extractable fraction which was 4-8 times greater than in the grassland. At both locations, the total inorganic fluoride levels in the top 30 cm of soil were constant. In contrast, the water-soluble inorganic fluoride levels increased with depth in grassland soils but decreased with depth in forest soils. The authors suggest that these differences are due to greater leaf area under the pine canopy, resulting in a higher rate of deposition. Different mobilities among the inorganic fluoride compounds and interactions of inorganic fluorides with aluminium and other organic ligands may also lead to distinct accumulation patterns.

The inorganic fluoride content of the organic portion in soil may reach high levels (*e.g.*, up to 0.44 mg F^-/g) (Perel'man 1977). The author postulated that high soil inorganic fluoride levels in some areas may result from plant uptake via the air and subsequent return to the soil as decayed vegetation. Inorganic fluoride levels are usually higher in samples from deeper horizons due to leaching from the more highly acidic surface horizons, where inorganic fluorides have a low affinity for organic material, and subsequent precipitation and retention by clay minerals and silts in the more basic deeper horizons (Davison 1983; Kabata-Pendias and Pendias 1984).

Elrashidi and Lindsay (1986) investigated whether the presence of a single inorganic fluoride-containing solid compound could account for the solubility of inorganic fluoride in various soil samples. Studies on the influence of aluminium fluoride, fluorite and fluorophlogopite ($KMg_3AlSi_3O_{10}F_2$) on the solubility of inorganic fluorides in strongly acidic, slightly acidic and alkaline soils showed that fluorophlogopite may be the compound primarily responsible for determining the solubility of inorganic fluorides in alkaline soils; however, no correlation could be identified in the other two soil types.

4.3 Aquatic Processes

Inorganic fluoride from the lithosphere enters the hydrosphere as a result of mineral leaching or atmospheric deposition to groundwater, lakes, and streams. Naturally occurring inorganic fluoride-rich waters usually originate from sub-surface sources, and are found in areas associated with volcanic activity or deposits of fluorite or phosphate-containing minerals (Fuge 1988). Inorganic fluorides generally pass from the hydrosphere into the atmosphere by vaporisation and aerosol formation (CPHA 1979). As with other halogens, inorganic fluorides transfer from the sea surface to the atmosphere typically in the form of aerosols. Soluble inorganic fluorides may form aerosols at the air-water interface or vaporise to the atmosphere (Brimblecombe and Clegg 1988), whereas undissolved species generally undergo sedimentation. Due to its lithophilic nature, the levels of inorganic fluorides in the hydrosphere and atmosphere are very low when compared to chlorides and bromides (Fuge 1988).

Factors determining the leaching of inorganic fluorides from minerals into ground and surface waters have been described by a number of researchers. The amount of inorganic fluorides leached is high at acidic pH and minimal at neutral pH, and is positively correlated with the silicic acid content of the water. The inorganic fluoride content of lake water is also associated with pH and is thus influenced by carbonate lithogies and acidification due to acid precipitation (Coker and Shilts 1979). In water, inorganic fluorides remain dissolved in solution under acidic conditions, low hardness, and the presence of ion-exchange material (*e.g.*, bentonite clays and humic acid), calcium or aluminium ions (Coker and Shilts 1979; Pickering et al. 1988; Sahu and

Karim 1989). Fluorides are important for mobilising aluminium into soluble complexes; at pH 5 and below, fluorides are almost entirely complexed with aluminium. As a consequence, free F^- levels are generally low (Skjelkvåle 1994a; Radic and Bralic 1995). Sahu and Karim (1989) surveyed inorganic fluoride levels in open and bore wells in the Amreli district of Gujarat, India, an area extensively covered by weathered basic lava flows. Analyses revealed that there is a positive correlation between alkalinity or low hardness of water and inorganic fluoride level, and suggested that the most probable source of inorganic fluorides is weathered Quaternary sedimentary rocks and micaceous clays.

5. ENVIRONMENTAL CONCENTRATIONS OF INORGANIC FLUORIDE

Environmental concentrations in water may vary significantly as they are influenced by a number of factors, including mineral deposits in the vicinity of the water body and proximity to anthropogenic sources. Inorganic fluorides are introduced into the aquatic environment by different pathways (Chapter 4), and consequently, all water bodies contain inorganic fluorides. Levels of Inorganic fluorides in aquatic biota are primarily influenced by water concentration, exposure time, water temperature and pH. Aquatic animals take up inorganic fluorides predominantly via drinking water. Environmental levels of inorganic fluorides in aquatic plants differ widely depending on species and availability of fluorides in ambient water.

5.1 Fluoride Levels in Precipitation

Levels of inorganic fluorides in precipitation have been reported for various Canadian locations during the 1970s and 1980s. Barnard and Nordstrom (1982) noted that earlier studies often reported erroneously high inorganic fluoride levels in precipitation due to the presence of dry fallout in samples, conducting studies near potential pollutant sources and inadequate analytical and statistical methods. The level of inorganic fluorides in precipitation is influenced by a number of factors, including proximity to natural or anthropogenic sources, amounts of other chemicals present in the atmosphere, meteorological factors such as wind speed and direction, amount of precipitation, and physical and chemical transformations in the atmosphere (Khwaja and Husain 1990).

Inorganic fluoride levels in rainfall were studied in the Kitimat region of BC (1980-81) at distances 1.2 to 5.6 km from an aluminium smelter. A pulp mill, in the same area, is also a potential emission source. Samples were collected using the lime plate method. In November 1980, during a storm, 58.4 mm of rain fell over a 2-d period, the inorganic fluoride levels averaged from < 0.04 to 0.07 mg F^-/L, while during another storm in May 1981 (May 13 - May 15), in which 10 mm of rain fell, the inorganic fluoride levels at five stations averaged from < 0.04 to 1.2 mg F^-/L (Kotturi 1990). In Wales, UK, levels of inorganic fluorides in rainwater samples collected over a 5 year period (1983-88) were highly variable, ranging from 0 to 0.230 mg F^-/L, with a mean flow/volume weighted concentration of 0.034 mg F^-/L(Neal et al. 1990).

In the Saguenay-Lac Saint Jean district of Quebec near two old Canadian aluminium smelters, levels of inorganic fluorides in snow from an area covering 4 500 km^2, were measured in 1978 and 1984 (Ouellet 1987). In 1978, elevated levels of inorganic fluorides were detected in a 3 000 km^2 area surrounding the aluminium smelters, but by 1984 elevated levels were restricted in a 100 km^2 area. In 1978, the average inorganic fluoride concentration in snow was 0.925 mg/L; n = 344 (detection limit [D.L.] = 0.02 mg/L) and detected concentrations exceeded the background concentration in an area 3 000 km^2 surrounding the aluminium smelters. By 1984, the average concentration had fallen to 0.097 mg/L; n = 194 (D.L. = 0.01 mg/L) due to the mandated installation of antipollution devices. The natural background concentration of inorganic fluorides is 0.05 mg/L.

Levels of inorganic fluorides in snow were measured 30 km north of Val d'Or, QC, over the Barvallée Deposit. The Barvallée Deposit is an area in the Abitibi greenstone belt where a large sulphide body of ore was found. Snow samples were analysed using a

fluoride electrode (D.L. = 10^{-10} mg/L) and inorganic fluoride content of the snow was found to be 0.001 - 0.042 mg F^-/L with an average of 0.005 mg F^-/L; n = 77 (Lalonde 1976). Two sources of inorganic fluorides in the snow were suspected: 1) formation of hydrofluoric acid by the reaction of sulphuric acid with fluorine-bearing minerals; and 2) diffusion of inorganic fluoride ions from the A-horizon of soil into the snow. The possibility of atmospheric contamination was not discussed. Singer and Armstrong (1977) reported inorganic fluoride levels of 0.03 to 0.04 mg F^-/kg in snow in the Twin Cities (Minneapolis and Saint Paul, MN, U.S.). In a non-industrialised wilderness region, they found that the level of inorganic fluorides in snow was below the detection limit. The detection limit of the method used was not given nor were the number of samples reported.

In 1977 and 1978, inorganic fluoride levels in both rain and snow were monitored in the area around a phosphorous fertiliser plant in Newfoundland (Sidhu 1982). Average inorganic fluoride levels in rain were 0.28 mg F^-/L at a distance of 1.4 km from the source and <0.01 mg F^-/L at 18.7 km. The average inorganic fluoride levels in snow ranged from 0.36 to 0.02 mg F^-/kg at distances of 1.4 and 18.7 km from the source, respectively. Eight rain samples at each station and seven snow samples per station were collected over the 30-d sampling period.

As mentioned, Barnard and Nordstrom (1982) studied background inorganic fluoride levels in two locations in the U.S. The first sampling site was located on the Atlantic coast, while the second was located inland. Neither of the sites were near a point source of inorganic fluorides. Background inorganic fluoride levels in precipitation at the inland sampling site were in the range of 0 - 0.018 mg F^-/L, with a mode of 0.009 mg F^-/kg and a median of 0.09 mg F^-/L; n = 34. For the coastal site, the range was 0 - 0.014 mg F^-/L with a mode of 0.003 mg F^-/L and a median of 0.0042 mg F^-/L; n = 33.

Khwaja and Husain (1990) analysed the major chemical components of precipitation from a site in Albany, NY, U.S. Inorganic fluoride content was measured using an ion selective electrode with a minimum detection limit of 0.00053 mg F^-/L. The monthly mean values for inorganic fluorides ranged from 0.00058 mg F^-/L in December to 0.0026 mg F^-/L in April; n = 142. The pH of precipitation (mean volume weighted) was 4.2. The highest inorganic fluoride level detected (0.0026 mg F^-/L) occurred in April. This high level may be related to the greater levels of soil dust and agricultural activity occurring during this time of the year. Factor analysis indicated that a major anthropogenic source for inorganic fluoride emissions was the burning of fossil fuels at coal-fired power plants, probably originating from the high sulphur emitting regions in mid-western U.S.

5.2 Fluoride Levels in Fresh Water

The mean inorganic fluoride level in fresh waters across Canada is 0.05 mg F^-/L (0.01 - 11.0 mg F^-/L, n = 51 299) (GSC 1991; Parker 1992). Inorganic fluoride levels in the Great Lakes range from 0.05 to 0.14 mg F^-/L (Warrington 1990). Levels of inorganic fluorides in surface waters in the Madoc area of south-central Ontario range from 0.060 to 0.420 mg F^-/L, with an average of 0.125 mg F^-/L.

The level of inorganic fluorides in surface waters is correlated with the presence of inorganic fluoride-containing mineral veins in the vicinity (Lalonde 1976). The upper limit of this range is in the vicinity of industrial activities. Although recent data identified

phosphate fertiliser production activities as a major source of inorganic fluorides to the Canadian aquatic environment, aquatic concentration data associated with these production activities are not available. Data are available, however, for other industrial sectors. Levels of inorganic fluorides in the Piskahegen River (Mount Pleasant, NB), 2.5 km downstream from an abandoned tungsten mine, averaged from 0.24 to 1.37 mg F^-/L (mean = 0.758 mg F^-/L) (Gauthier 1992). Inorganic fluorides in Big Meadow Brook (East Kemptville, NS), located 4 km downstream from an open pit tin mine tailings pond, contained levels as high as between 5.9 and 11.0 mg F^-/L (n = 7), and a mean concentration of 3.8 mg F^-/L (n = 48) between 1988 and 1991 (Parker 1992). Inorganic fluoride levels in the Kitimat River, BC, (downstream of effluent discharges from an aluminium smelter, a methanol plant, and pulp and paper mill) ranged from below detection (0.1 mg F^-/L) to 0.19 mg F^-/L (n = 32) (Warrington 1992). The mean inorganic fluoride concentration from 242 sites across Alberta was 0.12 mg F^-/L (n = 10 429; range of 0.05 - 0.95 mg F^-/L) (Alberta Environment 1992). In BC, the mean inorganic fluoride concentration from twenty-one sites was 0.22 mg F^-/L (n = 543; range = 0.10 to 0.71 mg F^-/L) (British Columbia Ministry of the Environment 1991).

According to the U.S. Geological Survey (1957), most rivers in the U.S. have natural inorganic fluoride levels in the 0.1 mg F^-/L range while some waters in the western regions contain greater than 1 mg F^-/L. Elevated inorganic fluoride levels are often seen in regions of geothermal or volcanic activity. For example, hot springs and geysers in Yellowstone National Park contained 25 - 50 mg F^-/L (Neuhold and Sigler 1960) while the Firehole and Madison Rivers, also in Yellowstone, contained from 1 to 14 mg F^-/L. Walker and Pyramid Lakes, Nevada, U.S., contained levels as high as 13 mg F^-/L (Sigler and Neuhold 1972). In China, levels in hot springs generally exceed 5.0 mg F^-/L, and in one spring an inorganic fluoride level of 45 mg F^-/L was observed (Fuhong and Shuquin 1988). In India, the inorganic fluoride level in surface waters lies in the range of 0 to 20 mg F^-/L, and was typically around 5 mg F^-/L (Bulusu and Nawlakhe 1988).

Sparks et al. (1983) monitored inorganic fluoride levels up to 12 times a year at two locations in the Illinois River (Marseilles and Valley City, IL). The highest level, 0.7 mg F^-/L, was recorded at Marseilles which showed consistently higher values than the Valley City monitoring site. This increase was attributed to discharges of fluoridated municipal water from the Chicago area. No mean values for either monitoring station, other than the highest value for the Marseilles location were reported.

Inorganic fluoride concentrations, ranging from <0.005 to 0.56 mg F^-/L, in Norwegian lake water are mostly caused by the fluoride content in bedrock (Skjelkvåle 1994a;b). In acidified areas in southern and south-western Norway, higher fluoride levels were measured in lake water than in regions of comparable geology. The author found a weak, but significant correlation between fluoride and SO_4^{2-}, indicating acidification in surface waters. Fluorides are important for mobilising aluminium into soluble complexes; at pH 5 and below, F^- is mostly complexed with aluminium, whereas at higher pH values, Al concentrations decrease and aluminium hydroxide is dominant relative to aluminium fluoride. Consequently, free fluorine ion levels increase at pHs greater than 5.

5.3 Fluoride Levels in Marine Water

The mean inorganic fluoride concentration in sea water is 1.3 mg F^-/L (Dobbs 1974; Connell and Airey 1982; Warrington 1990). Data on inorganic fluoride levels in sea water in Canada are limited. A study conducted in 1989 reported inorganic fluoride

concentrations in Kitimat Harbour, BC, ranging from 0.2 to 44.0 mg F^-/L (mean = 2.8 mg F^-/L; n = 40). Samples were collected at distances between 100 and 800 m from an aluminium smelter outfall (Warrington 1992). Samples collected between 1988 and 1990 at different locations in Kitimat Arm (within 2 km of an aluminium smelter, a methanol plant, and a pulp and paper mill) had inorganic fluoride concentrations that ranged from less than detection (0.1 mg F^-/L) to 1.3 mg F^-/L; (n = 69) (Warrington 1992). Samples collected in Kitimat Arm closer to an industrial outfall had mean inorganic fluoride levels of 0.012 mg F^-/L (0.001 to 0.069 x 10^{-3} mg F^-/L; n = 25).

The free and total inorganic fluoride concentrations in the Pamlico Estuary, NC, were measured with an ion selective electrode (Chamblee et al. 1984). To free complexed inorganic fluorides, samples were mixed with a buffer that adjusted the pH of the solution to approximately 5.5. This treatment of a sample will not necessarily release all inorganic fluorides from the matrix. An estimated 10.5% of the inorganic fluorides in the estuary water were complexed with ions such as Al^{3+} or Fe^{3+}. The authors reported the total inorganic fluoride concentration in the estuary ranged from 0.09 to 2.45 mg F^-/L; n = 93. The highest total inorganic fluoride concentrations occurred close to the Texas Gulf phosphate ore mining and processing facilities located on the south bank of the Pamlico Estuary.

5.4 Fluoride Levels in Groundwater

Possible pathways of inorganic fluorides include wet/dry deposition, and decomposition of fluoride-containing leaves. Consequently, inorganic fluorides are leached into groundwater. Levels of inorganic fluorides in groundwater vary considerably depending on the hydrogeological situation of the underlying bedrock. For example, in the Oyen area of Alberta, an analysis of the groundwater showed levels <1 mg F^-/L in bedrock waters and <0.5 mg F^-/L in drift waters (Borneuf 1979). Inorganic fluoride levels have also been measured in well water in a number of British Columbia locations. The average value was 0.414 mg F^-/L (range = 0.100 to 3.520 mg F^-/L) (British Columbia Ministry of the Environment 1991). Sahu and Karim (1989) surveyed the inorganic fluoride levels in open and bore wells in an area extensively covered by weathered basic lava flows in the Amreli district of Gujarat, India. While some dug wells and open tanks had levels of up to 1.1 mg F^-/L, the shallow groundwater varied in inorganic fluoride levels from < 1 to 7.6 mg F^-/L.

In one of the few studies, Lalonde (1976) found that water inorganic fluoride levels in 200 wells varied from 0.021 - 1.8 mg F^-/L in the Madoc area, Hastings county of south-central Ontario (arithmetic mean = 0.105 mg F^-/L). Contour maps of inorganic fluoride levels in the groundwater clearly delineated the major fluorite faults. Water-soluble soil inorganic fluorides also served as a good indicator of fluorite deposits. Lalonde (1976) noted that although there were no large seasonal variations in inorganic fluoride levels, heavy rainfall caused inorganic fluoride levels in groundwater to increase several fold. In the Abitibi area of Quebec, inorganic fluoride levels in groundwater varied from 0.02 to 1.2 mg F^-/L (average of 0.1 mg F^-/L) (Lalonde 1976). Levels of inorganic fluorides in the groundwater were high indicating veins of inorganic fluorides were present.

The highest recorded fluoride levels in Canada have been identified in groundwaters of the Maritime Carboniferous Basin in Moncton, Chipman, south of Fredericton, NB, and the Maria area in the Gaspé region, QC (Boyle and Chagnon 1995). Natural background fluoride levels in groundwater associated with the Carboniferous sediments are above

5 mg F⁻/L. The high fluoride levels in the water are due to physico-chemical processes including: 1) dissolution of the calcareous matrix; 2) Ca^{2+}, Mg^{2+}, K^{+}, Sr^{+} replacing Na^{+}, and with increasing pH, Ca^{2+} and Mg^{2+} decrease; and 3) water becomes a strong anion exchange medium (*i.e.*, Na-HCO_3-F waters). Fluoride-containing minerals like fluorite, apatite, and mica are more soluble in waters with low calcium concentrations, *i.e.*, soft water.

In other countries, elevated inorganic fluoride levels caused by the hydrogeology of the region have been studied. In areas of China where inorganic fluoride mineralisation can occur (*e.g.*, the Jiling, Quinghai, Hebei, and Shanxi Provinces), the level of inorganic fluorides in the groundwater is high, ranging from 1 to > 20 mg F-/L (Fuhong and Shuquin 1988). Deep groundwater (*i.e.*, semiconfined or confined water at a depth of > 30 - 60 m) could contain inorganic fluoride levels of about 1 mg F-/L in most areas, but can exceed 8.0 mg F-/L in some locations (Fuhong and Shuquin 1988).

5.5 Fluoride Levels in Aquatic Biota

No data could be located regarding environmental concentrations of inorganic fluorides in freshwater fish nor freshwater plants. Inorganic fluoride levels in biota are limited to marine organisms.

5.5.1 Aquatic Animals

Walton (1988) reviewed inorganic fluoride levels in marine organisms, particularly in krill and wildlife feeding on krill (*e.g.*, seals and adelaide penguins). Levels of inorganic fluorides in krill (*Euphausia superba*) are high: 0.33 mg F⁻/g for the whole animal, and 1.20 mg F⁻/g for the shells and cuticle (Sherlock 1984). Hempel and Manthey (1981) studied the inorganic fluoride level in krill larvae. Hauls were done at a maximum sampling depth of 200 m. Calyptopis stage I, the first active near-surface feeding stage, were the most abundant in the samples. The high levels of inorganic fluorides found (range = 1.46 to 1.73 mg F⁻/g dw (dry weight) and mean 1.59 mg F⁻/g dw were assumed to originate as a consequence of some mechanism which extracts and stores inorganic fluorides from sea water.

Concentrations in fresh adult krill was generally below 1.0 mg F⁻/g. Adelung et al. (1987) studied fluorides in tissues of two krill species (Antarctic *Euphausia superba* and the North Atlantic *Meganyctiphanes norvegica*) in relation to the moult cycle and found that although cuticle inorganic fluoride concentrations were high (2.6 mg F⁻/g dw and 3.3 mg F⁻/g dw, respectively), soft tissue (*i.e.*, blood, muscle) contained less than 0.006 mg F⁻/g dw. The results showed that fluoride accumulation in both species takes place in the cuticle. For example, in the euphausiids, over 99% of the total fluoride content was accumulated in the cuticle. For *E. superba* the mean fluoride content in the cuticle was 2.59 mg F⁻/g dw and 1.06 mg F⁻/g dw in the whole body. *M. norvegica* contained a mean content in the cuticle 3.34 mg F⁻/g dw, whereas the mean concentration in the whole body was 2.15 mg F⁻/g dw. Inorganic fluoride uptake in both species took place during the same physiological phase (*i.e.*, shortly after moult during cuticle growth). Thus, sodium fluoride is reaccumulated from the surrounding medium with regrowth (Adelung et al. 1987). The value for soft tissue is comparable to the level of inorganic fluorides in vertebrate tissue, disproving earlier assumptions that high levels found in krill organs indicated higher tolerance to inorganic fluorides. The higher values reported by other authors of earlier studies on krill soft tissue were probably the result of

contamination of the samples from cuticular fragments. Levels of inorganic fluorides in cuticle recorded by Adelung et al. (1987) were in the same range as reported previously. Given that the moult cycles of these krill average about 15 days, inorganic fluoride levels in the cuticle must increase from a postmoult concentration of less than 1.0 mg F^-/g dw to over 3.0 mg F^-/g dw in a very short time. Adelung et al. (1987) found no substantial variation from low basic levels in soft tissues throughout the moult cycle, indicating that if inorganic fluorides are taken up internally, there is a very efficient mechanism for sequestering it to the cuticle without allowing elevated levels to occur in the soft tissues. It is also likely that F^- is taken up by the cuticle from the external environment, as the majority of the inorganic fluorides being fixed into the cuticle occurs in the first two moulting stages when the food intake is reduced. This hypothesis was supported through experiments by Keck (1984) using starved specimens.

In another study, Adelung et al. (1985) examined tissue levels of three different Antarctic seals, the crabeater seal (*Lobodon carcinophagus*), the Weddell seal (*Leptochynotes weddelli*) and the Fur seal (*Arctocephalus tropicalis*) which feed on krill. The tissue levels of inorganic fluorides in these three seal species were similar those in non-krill-eating marine or terrestrial invertebrates. The soft tissue inorganic fluoride levels ranged from 2.3 to 9.1 mg F^-/g dw, with the lowest amounts found in adipose tissue, and the highest amounts in the brain. Levels in the blood were also low (0.006 mg F^-/g). Mean skeletal levels were 2.0 mg F^-/g in the Weddell seal (0.88 to 2.20 mg F^-/g), yet were considerably higher in the Crabeater seal (1.34 - 6.38 mg F^-/g). Mean levels in dentine were 2.3 mg F^-/g in the Crabeater seal and 2.4 mg F^-/g in the Weddell seal (Adelung et al. 1985). Very high inorganic fluoride levels (0.93 mg F^-/g for low tide sites and 1.17 mg F^-/g for mid-tide sites) were found in amphipods residing in sediment of interstitial water at the head of Kitimat Arm, BC, near a large aluminium smelter (Hocking et al. 1980). Similar results by other researchers showed that shrimp and prawns (*Palaemon pacificus* and *Penaeus indicus*) contained up to 3.0 mg F^-/g in ashed samples (Hemens and Warwick 1972)

Three species of mullet (*Mugil auratus risso*, *Mugil cephalus* L. and *Mugil labrosus*), caught in Gabes Bay, South Tunisia, (inorganic fluoride water levels about 2-3 mg F^-/L) contained tissue fluoride levels 4-5 times higher than fish from the Tunis Bay, which is remote from point-sources (inorganic fluoride water levels about 1.4 mg F^-/L) (Milhaud et al. 1981). Mean inorganic fluoride values in mullet species from Gabes Bay were 320 ± 225; 9.6 ± 10.2; and 14.6 ± 11.1 mg F^-/g wet weight (ww) for fish bone, muscle, and muscle + skin, respectively. Comparatively, the levels of controls were significantly lower: 73 ± 40.5; 1.8 ± 0.6; and 3.8 ± 1.6 mg F^-/g ww, respectively. The authors believed the relatively high standard deviation was due to differences in accumulation by fish. In addition, the skin, especially scales and fins, and skeleton also accumulate inorganic fluorides (British Columbia Ministry of Environment 1991).

In the vicinity of an aluminium smelter in Norway, a sea mollusk, Limpet (*Patella vulgata*) and two mussel species, the blue mussel (*Mytilus edulis*) and the horse mussel (*Modiolus modiolus*) were analysed for inorganic fluorides (Knutzen and Bokn 1987). Neither *P. vulgata* nor *M. edulis* were found to accumulate significant levels of inorganic fluorides, although *P. vulgata* had slightly increased levels amounting to about 10 - 20% over controls (0.005 -0.015 mg F^-/g dw), in both shell and soft tissues (levels not reported). Analytical results for *M. modiolus* were not presented.

Nell and Livanos (1988) conducted a series of experiments on juvenile rock oysters (*Saccostrea commercialis*) and flat oysters (*Ostrea angasi*) held for over 3 weeks in sea water. Oysters were tested over a range of exposure conditions: 15 to 45% salinity, 12 to 30°C, and inorganic fluoride levels up to 50 mg F^-/L. The levels of inorganic fluorides in rock oyster tissues correlated linearly to those in sea water. Accumulation of inorganic fluorides in rock oyster also increased with increasing water temperature. Exposure of the oysters to 50 mg F^-/L of inorganic fluorides resulted in tissue levels containing 1.12 mg F^-/g at 12°C, 1.14 mg F^-/g at 18°C, 2.28 mg F^-/g at 24°C, and 2.13 mg F^-/g at 30°C. Concentrations in whole dry rock oyster ranged from approximately 1 mg F^-/g at background inorganic fluoride levels (0.7 mg F^-/L) to approximately 0.21 mg F^-/g at 30 mg F^-/L. Increases in concentration occurred when temperatures increased from 18 to 24 and 30°C.

5.5.2 Aquatic Plants

Hocking et al. (1980) analysed samples of seaweed for their inorganic fluoride concentrations at sites nearby an aluminium smelter operating at the head of Kitimat Arm, BC. For seaweeds, *Fucus distichus* and *Ectocarpus* sp., inorganic fluoride concentrations were determined for both low and mid-tide sites at 150 and 500 m from the outfall. At low tide sites, *F. distichus* had values of 0.062 and 0.048 mg F^-/g, at 150 and 500 m, respectively. *Ectocarpus* sp. had a level of 0.143 mg F^-/g at 500 m from the outfall. *Ectocarpus* sp. had levels of 0.317 and 0.140 mg F^-/g at two mid-tide sites, 150 and 500 m respectively, while *F. distichus* L. had a level of 0.018 mg F^-/g 500 m from the outfall.

Murray (1981) studied the effects of elevated inorganic fluorides on an estuarine ecosystem in New South Wales, Australia. The study location was surrounded by three major sources of inorganic fluoride emissions. This location was characterised by a high frequency of temperature inversions (*i.e.*, increases in temperature with height), occurring at a frequency of 52 and 78% of sampling periods on summer and winter mornings, respectively. Marine vegetation contained mean levels of inorganic fluorides ranging from 0.131 ± 0.054 mg F^-/g dw in washed samples to 0.207 ± 0.077 mg F^-/g dw in unwashed samples. Other vegetation samples contained elevated inorganic fluoride levels, also. These results suggest that the rate of fluoride uptake is species-dependent.

6. BIOACCUMULATION AND BIOCONCENTRATION

Aquatic and terrestrial animals take up and accumulate inorganic fluorides from water and from food with the later being more important for fish, marine mammals and wildlife than for invertebrates (Hemens and Warwick 1972; Fleming et al. 1987; Neuhold and Sigler 1960; Wright 1977). Inorganic fluoride distribution is rapid in the body, blood and cell fluids. The extent to which fluorides are absorbed may be reduced by aluminium, phosphorous, magnesium or calcium. Approximately 99% of the body burden of fluorides is accumulated in bones and teeth, replacing hydroxyl groups in apatite (Ledbetter et al. 1960; WHO 1997). Inorganic fluorides are found also in soft tissue (Neuhold and Sigler 1960; Wright and Davison 1975; Wright 1977) and blood (*i.e.*, 75% of the fluoride level is in plasma and 25% in red blood cells) which serves as a transport medium for inorganic fluorides (WHO 1997). Terrestrial plants may accumulate inorganic fluorides, preferentially in their cell walls, from airborne deposition (*e.g.*, through leaves) and uptake from soil (Ledbetter et al. 1960; Davison 1983). Studies on the depuration kinetics of inorganic fluorides in both animal and plant species are equivocal. Urinary excretion appears to be the most important route in mammals (WHO 1997), while various routes have been postulated for plants (*e.g.*, decomposition, leaching by rain, and volatilisation) (Davison 1983).

Limited evidence in the literature suggests that inorganic fluorides do not biomagnify in natural aquatic or terrestrial food chains (ATSDR 1991). Some aquatic and terrestrial biota, however, bioaccumulate soluble inorganic fluorides (Hemens and Warwick 1972; ATSDR 1991). A terrestrial study conducted near a reclaimed fluorspar mining site revealed elevated inorganic fluoride levels in plants, invertebrates and small mammals compared to a control site (Andrews et al. 1982). Similarly, twenty-four hours after sodium fluoride was released into an experimental pond, the concentration of inorganic fluorides in aquatic vascular plants increased 35-fold. Increased concentrations were observed also for algae (14-fold), mollusks (12-fold), and fish (7-fold) (Kudo and Garrec 1983). In addition, fluorides can accumulate in dairy cows. A mineral supplement known as bone meal is used as a food additive for livestock and may contain high levels of fluorides. Cattle may accumulate 10 000 mg F^-/kg of bone compared to normal levels of 1 500 mg F^-/kg (Warrington 1990). Dairy cattle have been found to be the most sensitive livestock to fluoride toxicity as they have high food and water uptake rates and long productive lives. This results in the maximal opportunity for fluorides to accumulate to harmful levels in dairy cows and eventually end up in future generations.

6.1 Freshwater Fish and Invertebrates

One to three-year-old brown trout (*Salmo trutta*) from the Firehole River in Yellowstone Park, WI, where inorganic fluoride levels are 1 to 14 mg F^-/L, had inorganic fluoride levels of up to 1.6 mg F^-/g ww in their bones (Neuhold and Sigler 1960). The presence of inorganic fluoride in bone apatite promotes crystal growth and reduces the inclusion of carbonates. Bowser et al. (1988) found that accumulation of inorganic fluorides in bones of rainbow trout (*Oncorhynchus mykiss*) was insignificant at exposure levels of inorganic fluorides below 0.001 mg F^-/g. Other examples of inorganic fluoride accumulation in freshwater fish, *Salmo trutta* (brown trout), after long-term exposure in water are presented in Table 13.

Table 13. Inorganic Fluoride Accumulation in Freshwater Fish as a Function of Ambient Inorganic Fluoride Levels and Exposure Time

Fluoride mg/L	Exposure Medium	Duration	Species, Conditions, Accumulation Rate	Reference
1-14	River	1-3 a	• *Salmo trutta* (brown trout), Firehole River, Yellowstone Park • bone levels of up to 1.60 mg F^-/g in 1-3 year old fish	Neuhold and Sigler 1960
5	NaF	200 h	• *Salmo trutta* (brown trout); 2 cm • 12°C; pH 6.8 • hardness 73 mg $CaCO_3$/L • whole body levels of 0.010 mg F^-/g	Wright 1977
10	NaF	200 h	• *Salmo trutta* (brown trout); 2 cm • 12°C; pH 6.8 • hardness 73 mg $CaCO_3$/L • whole body levels of 0.020 mg F^-/g	Wright 1977
20	NaF	200 h	• *Salmo trutta* (brown trout); 2 cm • 12°C; pH 6.8 • hardness 73 mg $CaCO_3$/L • whole body levels of 0.030 mg F^-/g	Wright 1977

Source: Warrington (1990)

Freshwater fish including climbing perch (*Anabas testudineus*), snakehead (*Channa punctatus*), walking catfish (*Clarias batrachus*), catfish (*Heteropneustes fossilis*), and clown featherback (*Chitala ornata*) exposed to inorganic fluoride concentrations ranging from 6.9 to 52.5 mg F^-/L (the fluctuation in fluoride concentrations due to seasonal conditions) in a captive pond accumulated 0.23, 0.28, 0.35, 0.34, and 0.17 mg F^-/g fresh weight, respectively, in their bones (Samal 1994). Fish in the unpolluted control pond accumulated less fluoride with average concentrations from 0.002 to 0.008 mg F^-/g fresh weight.

Mishra and Mohapatra (1998) compared the fluoride content of bones in the Indian toad (*Bufo melanostictus*) from a contaminated site to that in toads from a control site. Fluoride concentrations in fore- and hind-limb bones were measured in male and female toads. At the contaminated site, males contained 3.0 mg F^-/g dry bone weight, while females contained 1.9 mg F^-/g dry bone weight. At the control site, fluoride bone content in females was slightly higher (0.3 mg F^-/g dry bone weight) than in males (0.2 mg F^-/g dry bone weight). The authors did not provide detailed information about the contaminated site.

6.2 Marine Fish and Invertebrates

Juvenile mullet (*M. cephalatus*) (50-55 mm) exposed to 6.0 mg F^-/L for 68 days contained a total fluoride body concentration of 0.796 mg F^-/g ash, whereas the control group contained a lesser concentration of 0.422 mg F^-/g ash (Hemens et al. 1975). Fish of 16-18 mm contained 1.394 mg F^-/g ash, while the control group contained only 0.377 mg F^-/g ash, indicating a 57% larger bioaccumulation in the group of smaller fish (Hemens et al. 1975). This may be due to the ratio of hard to soft tissue or greater growth rates. In another experiment, Hemens and Warwick (1972) found a mean total

body fluoride concentration of 7.748 mg F^-/g ash in juvenile mullet (*M. cephalus*) after an exposure to 52.0 mg F^-/L for 72 days, whereas the control fish contained 0.1418 mg F^-/g ash.

In studies performed using marine invertebrates, substantial body burdens of inorganic fluorides were evident. Blue crabs (*Callinectus sapidus* Rathbum) kept in unpolluted sea water (0.5 - 1.5 mg F^-/L) had tissue concentrations of 0.298 mg F^-/g dw in the exoskeleton, 0.253 mg F^-/g dw in the gills, 0.0022mg F^-/g dw in the hepatopancreas, and 0.001 mg F^-/g dw in muscle tissue. Barbaro et al. (1981) studied the accumulation of inorganic fluorides in barnacles, *Balanus amphitrite*, and the mussel, *Mytilus galloprovincialis*, in a lagoon in Venice, Italy. Both organisms accumulated inorganic fluorides in their soft tissues, with maximum concentrations reaching 0.081 ± 0.006 mg F /g in barnacles and 0.085 ± 0.02 mg F^-/g in mussels. The bioconcentration factor, (ratio of mean concentration of inorganic fluorides in dry soft tissue as compared to mean concentration of inorganic fluorides in water) was between 20 and 70 for both species. Significant seasonal variation in the level of inorganic fluorides was observed in both barnacles and mussels and assumed to be related to various stages in the reproductive cycle of the organisms, with the highest level occurring during spawning. No explanation was provided for this observation, although the authors cite two other studies (see Simpson 1979; Francescon et al. 1980) in which a similar phenomenon was observed.

High inorganic fluoride levels in enameloids of fish (bones consisting of fluoroapatite) can have phylogenetic significance (Miake et al. 1991). The morphological features in the elasmobranch enameloid and its crystalline structure have been ascribed to their high inorganic fluoride content. Fluoridated carbonatoapatite in shark enameloid contained 0.0025 mg F^-/g during early development, and the crystals have a distinctive equilateral hexagonal shape. Dogfish enameloid has an isodiametric hexagonal cross section whereas teleost enameloid resembles enamel with a ribbon-like shape. During the developmental stages in bony fish, incorporation of inorganic fluorides is minimal and the enameloid has a ribbon-like structure; however, as mineralisation increases so does the incorporation of inorganic fluorides. This changes the morphology to equilateral hexagonal cross section shaped crystals. These effects demonstrate the action of fluoride ions as accelerators of crystal growth of fluoroapatite *in vivo* (Miake et al. 1991).

At inorganic fluoride levels of 52 mg F^-/L in water, prawns (*Penaeus indicus*), small mudcrabs (*Tylodiplax blephariskios*), and sand shrimps (*Palaemon pacificus*) have whole animal (ash) concentrations of 3.25, 1.41, and 3.12 mg F^-/g, respectively (Hemens and Warwick 1972). An unspecified species of oyster accumulated inorganic fluorides when exposed to levels over 2 mg F^-/L (Moore 1969). As barnacles accumulate inorganic fluorides in direct proportion to the ambient inorganic fluoride level, they are good bioindicators of inorganic fluoride pollution (Barbaro et al. 1981).

Wright and Davison (1975) studied accumulation of inorganic fluorides in a number of marine and intertidal animals situated close to an aluminium smelter in Lynewouth, Northumberland, England, that discharges an inorganic fluoride-containing effluent into the sea. Sea water in the region was found to be 0.0018 mg F^-/L above background levels (*i.e.*, in the order of 0.0034 mg F^-/L). The skeletal tissue of both vertebrates and invertebrates was found to have high inorganic fluoride levels and elevated amounts were also seen in the skin of some fish species. The exoskeleton concentrations for the swimming crab (*Portunus depurator*), shrimp (*Crangon vulgaris*) and prawn (*Leander*

serratus) were 0.0116 ± 0.0056, 0.0115 ± 0.0053, and 0.0113 ± 0.0068 mg F^-/g ww, respectively. Tissue accumulation of inorganic fluorides was highest in the skin (0.0296 mg F^-/g ± 0.0192) for cod (*Gadus morrhua*); in haddock (*Gadus aeglefinus*) and dabs (*Pleuronectes platessa*) the tissue accumulation was highest in the axial skeleton, 0.0493 mg F^-/g ± 0.0244 and 0.0997 mg F^-/g ± 0.1123 ww, respectively. Although the mechanism of accumulation in fish scales is not known, the authors suggest that some inorganic fluorides may be incorporated directly from the sea water.

6.3 Aquatic and Semi-Aquatic Animals (Mammals and Birds)

Wild bird populations are exposed to inorganic fluorides from natural and industrial releases. Uptake is mainly by consumption of food and drinking water. Fluoride accumulation in birds occurs mostly in bones and eggshells (Fleming 1996). For example, 99.5% of the fluoride content is stored in the skeleton of ducks (Culik 1987).

Vikøren and Stuve (1995) compared bone fluoride concentrations in Canada geese (*Branta canadensis*) to areas in Norway with levels of fluorides at impacted sites. Birds in the reference group (*i.e.*, not exposed to any industrial fluoride output) contained fluoride levels of 1.34 mg F^-/g bone ash dw. Groups from polluted sites contained levels of 3.37 and 1.45 mg F^-/g bone ash dw. The birds from polluted sites did not show gross osteofluorotic lesions. The authors concluded that Canada geese are not well suited as bioindicators for inorganic fluoride monitoring, because age assessments of birds are difficult due to alterations in nesting places, and as well as background concentrations of fluorides vary over wide ranges.

Fluoride exposure and accumulation in herring gulls (*Larus argentatus*) and common gulls (*Larus canus*) have been investigated by Vikøren and Stuve (1996). The authors examined eggs of both species from breeding colonies (Karmøy and Sunndal) exposed to fluoride emissions, and from reference sites (*i.e.*, no fluoride outputs) in Norway. Fluoride concentrations in egg shells from exposed sites were significantly elevated for both species in comparison to those from reference sites. For the common gull, the concentration in the egg shells for the two contaminated sites ranged from 0.137 to 0.212 mg F^-/g while those at the reference site ranged from 0.85 to 0.128 mg F^-/g. For the herring gull, levels ranged from 0.120 to 0.195 mg F^-/g at the contaminated site while the range was 0.83 to 0.143 mg F^-/g at the reference site. The last-laid egg (usually three/clutch) always showed the highest fluorine levels for both species. Vikøren and Stuve (1995) found a relationship between sex and fluoride accumulation; female gulls had significantly higher fluoride levels than males. A positive correlation between fluoride concentration in femurs of breeding female birds and in the shell of their eggs could be identified. Differences in egg volume, shell thickness, percent fertilised eggs, and changes in the morphology of bones (due to high fluoride levels in gull bones) could not be found.

The potential for inorganic fluorides to accumulate in birds is species dependant, and may relate, in part, to differences in anatomy. Adélie penguins (*Pygoscelis adeliae*) feeding naturally in the wild can tolerate higher levels to inorganic fluorides in their food (krill) than those fed food innoculated with NaF during laboratory feeding experiments (Culik 1987). Up to 68% of the fluorides in krill is available compared to NaF (100%). The author hypothesised that the inorganic fluorides in the krill is not readily available for uptake because it is primarily sequestered (99%) in the cuticle (exoskeleton) of this invertebrate. Although the penguins consume whole krill, they are unable to digest

chitinous cuticle because they lack a caecum. In contrast, mallard ducks, chickens and rats, all of which possess a caecum, the availability of fluorides from krill is about equal to that of NaF (reviewed in Culik 1987). The author attributed some of the difference in uptake results between penguins (feed fresh krill) and ducks (feed frozen krill) to redistribution of fluorides from the cuticle to the soft tissue during storage.

Bioaccumulation due to food intake and a significant positive correlation between high fluoride concentrations in bone tissue and age were observed in fin whales (*Balaenoptera physalus*) of the North Atlantic (Landy et al. 1991). The authors examined fluoride concentrations in ashed bone samples in 1982 and 1985. Whales seem to be tolerant to very high fluoride concentrations, as bone tissue of fin whales contained extremely elevated levels (1982: mean concentrations of 8.30 mg F^-/g dw in ashes samples of vertebral bone; 1985: mean concentrations of 9.80 mg F^-/g dw in ashes samples of vertebral bone) with no apparent toxic response. Stomach contents of the whales were analysed. The partly digested krill had a mean fluoride concentration of 2.23 mg F^-/g. No relationships between the variable body length or sex and fluoride concentration in the fin whales could be identified.

6.4 Aquatic Plants

Rooted vascular aquatic plants may accumulate and assimilate compounds from their environment from the water column, through submerged shoots, or from interstitial water of the sediments through the roots (Denny 1972). Although there is no detailed literature about the uptake mechanisms of fluorides by aquatic plants, the principal uptake procedure may be similar to uptake by terrestrial plants. In general, fluorides are taken up by terrestrial plants from the soil by passive diffusion, before being transported to the shoot by transpiration. Fluorides are also taken up from the air. For example, gaseous fluorides enters plant leaves though stomatal pores. Metabolic processes may be initiated by fluorides entering internal leaf tissues or deposited on active surfaces (*i.e.*, stigmata). About 60% of the total fluoride amount in a leaf may be superficial deposits.

Some plants accumulate inorganic fluorides while others do not (Samecka-Cymerman and Kempers 1990). In general, the rate of accumulation from ambient water to marine plants is far lower than that of airborne inorganic fluorides by land species (Hocking et al. 1980). Fluoride uptake by aquatic plants appears to be positively correlated to fluoride concentration in water and to the duration of exposure to fluorides (Kabata-Pendias and Pendias 1984; Shirke and Chandra 1991). For example, a positive relationship between fluoride levels in water and fluoride concentrations in aquatic liverwort (*Scapania undulata* (L.) *Dum.*) was observed by Samecka-Cymerman and Kempers (1990). Shirke and Chandra (1991), found a positive correlation between the accumulation of sodium fluoride in duckweed (S. *polyrrhyza*) and fluoride concentrations. Duckweed exposed to a water concentration of 10 mg F^-/L accumulated 0.40 mg F^-/g dw after 24-h and 0.45 mg F^-/g dw after 360-h. At a water concentration of 25 mg F^-/L, plants accumulated 1.03 mg F^-/g dw after 24-h and 1.07 mg F^-/g dw after 360-h.

Exposure of freshwater and marine plants to 100 mg F^-/L inorganic fluoride led to a 50-fold increase in inorganic fluoride concentration in tissues, while a 14-d exposure to 20 mg F^-/L led to a 38-fold increase (Marier and Rose 1971). Water hyacinths

(*Eichhornia crassipes*) absorbed inorganic fluoride efficiently at levels above 10 mg F^-/L in water (Rao et al. 1973).

No significant accumulation of fluorides in plant material could be detected in a test simulating the natural estuarine trophic conditions of a bay in South Africa. Seagrass (*Zostera capensis*) exposed to 52.0 mg F^-/L for 72 days contained 0.0186 mg F^-/g ash dw in roots, whereas the control group contained 0.0166 mg F^-/g ash dw (Hemens and Warwick 1972). Knutzen and Bokn (1987) analysed the level of inorganic fluorides in the marine benthic algae, bladder wrack (*Fucus vesiculosus*), knotted wrack (*Ascophyllum nodosum*), and seaweed (*Laminaria digitata*) in a fjord in Norway. Levels of inorganic fluorides in algae (650 m from the discharge area) were 5 to 15-fold greater than levels in control algae, *i.e.*, approximately 0.02 - 0.03 mg F^-/g dw. A 5-fold increase in inorganic fluoride levels over controls represents, at maximum, a doubling of the ambient water inorganic fluoride level, which was 2.4 - 5.9 mg F^-/L at two sites 100 m from the discharge area.

7. EFFECTS ON AQUATIC ORGANISMS

Inorganic fluorides are toxic to aquatic organisms and may cause adverse biological effects such as changes in blood composition, changes in carbohydrate and protein metabolism, reproduction impairment, reduced embryonic and developmental life stage, and alterations in size and growth (*e.g.*, growth inhibition in aquatic animals and plants such as freshwater algae species). In addition, inorganic fluorides are neurotoxic causing adverse effects on the central nervous system. Furthermore, behavioural disruptions and adverse effects on the behaviour of aquatic organisms (*e.g.*, fish) have been reported.

Sodium fluoride (NaF) is the most common inorganic fluoride used in the aquatic toxicology studies discussed throughout this report; however, one report by Sanders and Cope (1966), studied cryolite (Na_3AlF_6). Toxicity studies with fluoride-containing effluent include Woodiwiss and Fretwell (1974), Damkaer and Dey (1989), Camargo (1991a), Camargo (1992), and Samal (1994).

7.1 Mode Of Action

Inorganic fluorides act as enzyme activity inhibitors in aquatic biota by blocking important enzyme processes (Angelovic et al. 1961; WHO 1997). Fluorides act *in vivo* and *in vitro* on enzymes, thereby affecting glycolysis, respiration, photosynthesis and other synthesis in plants, such as glucose 6-phosphate dehydrogenase, enolase, succinic dehydrogenase, catalase, cytochome oxidase, ATPase activity and transport, ATP activity of the plasma membrane, the chloroplast coupling factor, and more (NAS 1971; Miller 1997). The formation of metal-fluoride complexes may be one of the reasons for the inhibitory effect of inorganic fluorides (NAS 1971). With increasing fluoride intoxication aquatic biota need an abundance of calcium and magnesium to sustain their enzyme activities.

Inorganic fluorides may have a negative effect on glycolysis, which is imperative for CNS (central nervous system) functioning (ATSDR 1991). Limited neurotoxicological studies for aquatic animals are available, more studies exist for mammals. Mullenix et al. (1995) investigated neurotoxic effects of sodium fluoride on rats. Behaviour, body weight, and fluoride levels in plasma and brain of Sprague-Dawley rats exposed to sodium fluoride were compared to those of reference rats not exposed to the contaminant. The authors found positive relationships between exposure to sodium fluoride and behavioural disruption in the rat. Effects on rat behaviour were directly related to plasma fluoride levels and fluoride concentration in the brain. Fluoride levels in plasma predicted effects on behaviour, but not fluoride levels of exposure. The behaviour of aquatic animals, such as salmon migration, is affected by high fluoride concentrations (ranging between 0.2 and 0.5 mg F^-/L) in water (Appendix B1) (Damkaer and Dey 1989).

By inhibiting enzyme activity, inorganic fluorides impact many enzyme-based processes (Reddy et al. 1989). Freshwater crab (*Barytelphusa guerini*) exposed to 13.57 mg F^-/L for 15 days exhibited changes in carbohydrate metabolism, and a decrease in glycogen levels, while phosphorylase activity increased. Succinate dehydrogenase was inhibited in gills, muscle, and the hepatopancreas. Lactate dehydrogenase (LDH) was inhibited which led to an accumulation of lactate in tissues. Significant alterations in protein metabolism on acetylcholinesterase activity and oxygen consumption in freshwater crab

(*Barytelphusa guerini*) have been described by Reddy and Venugopal (1990a;b). Exposure to sublethal levels of 13.57 mg F^-/L for 15 days led to a marked depletion of total protein and free amino acid content. Values for aspartate aminotransferase (AAT), the key enzyme of nitrogen metabolism and energy mobilisation in invertebrates, alanine aminotransferase (ALAT), and glutamate dehydrogenase (GDH), a mitochondrial enzyme were elevated. The authors suggested possible compensatory mechanisms under fluoride intoxication.

In prokaryotic cells, inorganic fluorides are not mutagenic (WHO 1984; Health Council of the Netherlands 1990; ATSDR 1991; WHO 1997); however, increases in the frequency of mutations at specific *loci* in cultured mouse lymphoma and human lymphoblastoid cells have been observed and are most likely caused by chromosomal damage (WHO 1997). Evidence indicates that fluorides may produce chromosome aberrations and gene mutations in cultured mammalian cells. Literature regarding *in vivo* cytogenetic studies are contradictory, as some report an increase of chromosome aberrations when mammalians were exposed to fluorides, while other studies do not. No literature was available dealing with mutagenic effects in aquatic biota (Zeiger et al. 1993).

Haematological effects caused by exposure to inorganic fluorides have been observed in aquatic animals (Kaplan et al. 1964; Sigler and Neuhold 1972; Mishra and Mohapatra 1998). In the blood of rainbow trout (*Oncorhynchus mykiss*) and carp (*Cyprinus carpio*) the level of total serum protein drops and the gamma and beta globulins appear to change following exposure to inorganic fluorides. Serum alkaline phosphatase activity and plasma magnesium levels increase, while calcium decreases with increasing fluoride intoxication. As such, fish require more Ca^{2+} to compensate for changes in blood. Where there is a surplus of Ca^{2+}, Ca^{2+} may also serve as a protective agent against fluoride toxicity by binding to the soluble reactive fluoride ions and precipitating as calcium fluoride, which is a less toxic compound to biota (Neuhold and Sigler 1960; Pimentel and Bulkley 1983). In addition to Ca^{2+}, F^- may also bind with Mg^{2+} forming MgF_2 (Oliveira et al. 1978; Pimentel and Bulkley 1983; Smith et al. 1985). These chemical precipitation reactions occur in water and blood of aquatic biota because water and blood are the main transport medium of inorganic fluorides within an animals body. With increasing fluoride intoxication, the serum protein concentration, number of red blood cells (RBCs) or erythrocytes, blood haemoglobin and haematocrit decrease (Kaplan et al. 1964; Mishra and Mohapatra 1998). Red blood cells containing haemoglobin are responsible for the transport of oxygen to body tissues; therefore, a decrease of RBCs has negative consequences on animal respiration. An intoxication of CO_2 can provoke the death of an animal.

Besides calcium, other protective agents against fluoride toxicity have been studied. Selenium was researched by Pang et al. (1996). The authors looked at the influence of sodium fluoride on skeletal muscle by *in vitro* exposure of a four month old rat foetus skeletal muscle specimen to water containing selenium. Skeletal muscle cells were damaged, but less so for the group exposed to sodium fluoride and selenite. This protective effect of selenium may be due to improved mitochondrial membrane stability. In an *in vivo* study, rats consumed water containing 221 mg/L sodium fluoride, or 221 mg/L sodium fluoride and 16.7 mg/L sodium selenite for eight weeks (Pang et al. 1996). Fluoride treated water resulted in approximately a 27% decrease in activities of the enzyme succinate dehydrogenase, cytochome oxygenase, and Mg^{2+}-adenosine triphosphate. In the presence of selenium, enzyme activities declined approximately 17%. The results of these *in vivo* and *in vitro* studies demonstrated that fluoride can

damage skeletal muscle cells with necrosis following a disruption of energy metabolism in the mitochondrial membrane. There is no literature on aquatic biota available on this topic; however, similar effects are expected because the histochemistry of terrestrial and aquatic animals are comparable and fluorides are enzyme inhibitors in fish.

Neuhold and Sigler (1962) found chlorides can protect against the toxicity of fluorides to rainbow trout. One group of rainbow trout was tempered to chloride, the other group was not. The adverse response to fluoride was significantly reduced in the group of tempered fish compared to the group of non-tempered fish: 32 and 34% of tempered fish and 67 and 65% of non-tempered fish died when exposed to levels of 13 and 25 mg F^-/L, respectively. In both cases, increasing concentrations of fluoride caused an increase in fish mortality. Although, the LC_{50} was found to differ significantly as 6 mg F^-/L elicited a response from 50% of the non-tempered fish whereas 22 mg F^-/L was required for the tempered fish. The authors reported an increase in mucous cell production in gill epithelium, a reaction of secretion mechanism to elevated fluoride and chloride levels in water.

Fluoride toxicity to plants may be enhanced by the presence of aluminium. The combined toxicity of $AlCl_3$, AlF_3, NaF, and $AlCl_3$ and NaF was tested on prokaryotic cyanobacterium (*Nostoc linckia*) and the eucaryotic green alga (*Chlorella vulgaris*). AlF_3 and the combination of $AlCl_3$ and NaF are more toxic than all other substances. The toxicity of aluminium and fluorides to aquatic plants appears to increase with decreasing pH (Husaini et al. 1996; Rai et al. 1998). Additive interaction of $AlCl_3$ and NaF at pH 7.5 and 6.8, and synergistic interaction at pHs 6.0 and 4.5 have been observed. The toxicity of sodium fluoride in combinations with cadmium, cobalt, iron, manganese, tin, and zinc have been tested, but the combination of sodium fluoride with aluminium were found to be the most inhibitory (Husaini et al. 1996). The toxic effect of sodium fluoride in combination with aluminium is due to the complexation of fluoroaluminate (AlF_4^-), a structural analogue of PO_4^-, which affects negatively all the phosphate-associated enzyme activities.

In another study on the effects of toxicity of fluoride and aluminium on enzyme activities, Rai et al. (1998) exposed green alga (*Chlorella vulgaris*) to combinations of $AlCl_3$, AlF_3, NaF and $AlCl_3$ and AlF_3 at various pH levels. LC_{50}s for *C. vulgaris* at pH 6.8, 6.0 and 4.5 for AlF_3 were 86, 10, and 6 mg F^-/L, respectively, and for NaF 380, 266, and 133 mg F^-/L, respectively. Consequently, the toxicity for AlF_3 is greater than that for NaF. Again, an additive interaction of $AlCl_3$ and NaF at pH 6.8 and synergistic interaction at pH 6.0 and 4.5 was observed. The authors reported an inhibition in growth of 56% (AlF_3), 53% ($AlCl_3$), and 55% (NaF) at pH 6.8 and 58% (AlF_3), 53% ($AlCl_3$), and 50% (NaF) at pH 6.0. The uptake of nutrients as well as the enzyme activities, such as acid phosphatase, alkaline phosphatase, and ATP activity (synergistic inhibition at pHs 4.5 and 6.0; additive inhibition at pH 6.8) decreased. Fluoroaluminate (AlF_4^-) was formed in the medium and algal cells.

Fluoride itself acts as a protective agent against aluminium toxicity in aquatic animals. The influence of fluoride on aluminium toxicity to Atlantic salmon (*Salmo salar*) has been studied by Hamilton and Haines (1995). Alevins were exposed to various aluminium and fluoride concentrations at pH 5.5 and 6.5. At both pH levels gill filaments and secondary lamellae were swollen and thickened, but fluoride and aluminium toxicity to alevins appeared to be more elevated at pH 5.5 than pH 6.5. Fluoride concentrations (<100 mg F^-/L) may reduce morphological gill damage in fish exposed to aluminium in

acidic waters (*e.g.*, pH 5.5), whereas high fluoride concentrations (>100 mg F^-/L) may not reduce aluminium-induced effects. Parkhurst (1987) and Parkhurst et al. (1987) studied aluminium toxicity, fluoride concentration and the influence of chemical and physical parameters such as temperature, DOC and pH value in brook trout (*Salvelinus fontinalis*). Fluoride and temperature accounted for 1 - 2% of the variation in survival. The formation of a mixed ligand (F-Al-L-gill) complex at the gill surface was suggested by the authors. The effect of fluoride complexation on aluminium bioconcentration is presented in detail in other studies (Wilkinson et al. 1990; Wilkinson and Campbell 1993).

By inhibiting enzymatic activity, inorganic fluorides protect against bacterial kidney disease (BKD). Atlantic salmon (*Salmo salar*) with elevated prevalence of BKD were fed diets laden with fluorides. Results indicate that a diet with an elevated fluoride content can help control the illness (Lall et al. 1985). Bowser et al. (1988) calculated the positive correlation between BKD in rainbow trout and dietary fluoride. Following exposure to inorganic fluorides for 30 days at 15°C and at less than 50 mg $CaCO_3$/L water hardness, the incidence of BKD and consequently mortality on trout was substantially reduced. The authors suggested that inorganic fluorides inhibit the enzymatic activity of *Renibacterium salmoninarum*, the organism responsible for BKD, and thus prevented the initiation of infection (Bowser et al. 1988). Overall, a LC_{50} of 102 mg F^-/L was determined. No adverse effects were seen in fish exposed to inorganic fluoride levels up to 0.016 mg F^-/g ww.

Inorganic fluoride toxicity is negatively correlated to water hardness and positively correlated to temperature (Neuhold and Sigler 1960; Pimentel and Bulkley 1983). For example, water hardness (*i.e.*, Ca^{2+} concentration) has a considerable influence on the susceptibility of fish to inorganic fluorides. Hard water protective activity is two-fold: first, calcium in the ambient water may complex fluorides, rendering them unavailable for uptake; and, second, hard water may serve as a calcium reservoir for fish to augment systemic calcium levels that have been depleted as a result of inorganic fluoride intoxication. The latter helps maintain normal enzyme functioning (Sigler and Neuhold 1972; Pimentel and Bulkley 1983). For rainbow trout, Pimentel and Bulkley (1983) demonstrated that the LC_{50} was linearly correlated to total water hardness. The researchers noted that as much as 30% of the inorganic fluoride precipitated out in very hard water (385 mg $CaCO_3$/L at 12°C).

Exposure of rainbow trout yearling to sodium fluoride in a water hardness of 12 mg $CaCO_3$ results in a 21-d LC_{50} of 8.5 mg F^-/L (Herbert and Shurben 1964). Three different levels of water hardness were tested: 12, 45, and 320 mg $CaCO_3$/L. With increasing water hardness a precipitate formed and the amount of fluoride in solution varied. Herbert and Shurben (1964) concluded that dissolved fluoride in hard water is less toxic than in soft water. Experiments by Smith et al. (1985) examined the relationship between the fluoride toxicity (LC_{50}) and water hardness and found that rainbow trout and fathead minnows appear more sensitive to fluoride toxicity than do sticklebacks. Stickleback (*Gasterosteus aculeatus*) had 96-h LC_{50} values of: 340 (water hardness 78 mg $CaCO_3$/L), 380 (water hardness 146 mg $CaCO_3$/L), and 460 mg F^-/L (water hardness 300 mg $CaCO_3$/L). Trends observed for fathead minnow (*Pimephales promelas*) were reported as: 96-h LC_{50}s of 315 (water hardness 20 - 48 mg $CaCO_3$/L), 315 (water hardness 10 - 44 mg $CaCO_3$/L), 180 (water hardness 92 mg $CaCO_3$/L), and 205 mg F^-/L (water hardness 256 mg $CaCO_3$/L). For rainbow trout, the authors

determined a 96-h LC_{50} of 200 mg F^-/L (water hardness 23 - 62 mg $CaCO_3$/L). Lower concentrations, however, can be tolerated without ill effects (Smith et al. 1985).

Fieser et al. (1986) noted positive linear relationships between mortality and temperature when studying the effect of fluorides on survival and reproduction of *Daphnia magna*. At 15, 20, and 25°C, LC_{50} values were 335, 284, 220 mg F^-/L, respectively for total fluorides and 304, 251, 200 mg F^-/L, respectively for ionic fluoride. Median water hardness in this study was 169.3 mg $CaCO_3$/L. Similarly, Neuhold and Sigler (1960) found a positive linear relationship between mortality for rainbow trout eggs and temperature in soft water (7.5 mg $CaCO_3$/L). LC_{50} values were estimated between 222 to 273 mg F^-/L at 7.7°C, between 242 to 261 mg F^-/L at 12.7°C, and between 237 to 281 mg F^-/L at 15.5°C. Increases in temperature, and hence in the metabolic rate, led to linear increases in the toxicity of the inorganic fluoride. Angelovic et al. (1961) tested fluoride toxicity to rainbow trout at three different temperatures in (unspecified) soft water. The authors determined graphically LC_{50}s between 5.9 and 7.5 mg F^-/L for 7.2°C, between 2.6 and 6.0 mg F^-/L for 12.8°C, and between 2.3 and 7.3 mg F^-/L for 18.3°C.

There are no studies available dealing with an explicit correlation between the inorganic fluoride concentration and pH levels for fish and other aquatic biota, although free F^- levels are known to increase with increasing pH. Two separate mechanisms are described here: a) free F^- levels increasing with increasing pH, and b) increasing pH with increasing fluoride. Skjelkvåle (1994a;b) found a significant correlation between fluoride and SO_4^{2-} indicating acidification in surface water, free fluoride levels increase at pH ranges higher than 5.

Toxicity tests on brown trout (*Salmo trutta*) fry (Wright 1977) showed a positive linear relationship between mortality and exposure time in hours for a given fluoride concentration, water hardness and temperature. Increased toxicity with increased exposure time was also studied by Camargo and Tarazona (1991). The authors found 120-, 144-, 168- and 192-h LC_{50}s in soft water (ranging 21.2 to 22.4 $CaCO_3$) of 92.4, 85.1, 73.4, and 64.1 mg F^-/L, respectively, for fingerlings of rainbow trout and 135.6, 118.5, 105.1, and 97.5 mg F^-/L, respectively, for fingerlings of brown trout. These experiments demonstrate clearly the positive relationship between the toxicity of sodium fluoride and exposure time and the sensitivity to inorganic fluorides.

Other important factors affecting species sensitivity to inorganic fluorides include life-stage, physiology and exposure duration. These relationships will be exemplified in the following sections.

7.2 Toxicity to Freshwater Fish

The initial phase of acute inorganic fluoride intoxication in freshwater species such as rainbow trout and carp is characterised by apathetic behaviour accompanied by anorexia (Neuhold and Sigler 1960; Sigler and Neuhold 1972). Death may be preceded by initial lethargy, violent aimless movement and a loss of equilibrium, with death ultimately occurring as a state of partial or total muscle contraction (tetany). Similar symptoms of acute fluoride intoxication (*e.g.*, rupturing in vitelline membrane or a coagulation of the yolk protein) have been observed in rainbow trout embryos (Neuhold and Sigler 1960; Sigler and Neuhold 1972). In many cases, the surviving young fish had

curved spines (Sigler and Neuhold 1972). At sub-lethal concentrations, toxicity to rainbow trout is characterised by a darkening of the skin, hypoexcitability and a decreased respiratory rate (Landy 1989; Camargo and Tarazona 1991). Rainbow trout eggs hatch earlier at high fluoride concentrations, and a negative linear relationship exists between inorganic fluoride concentration and hatching time at doses between 0 - 300 mg F^-/L (Neuhold and Sigler 1960).

Key biotic parameters for toxicity of fluorides to freshwater fish are life stage, size of fish, physical condition and species. For example, fry are more sensitive to inorganic fluorides than larger individuals, and fish in poor physical condition are more sensitive than healthy fish.

Fry that have just finished feeding on their yolk sac, fingerlings, and juveniles are the most sensitive to fluoride uptake (*i.e.*, via consumption of water and food). In contrast, eggs and fry feeding on their yolk sac are less sensitive to fluorides because they are not directly exposed to fluorides though consumption of contaminated food. Rainbow trout eggs and fry in a static toxicity test with renewal, ambient temperature of 13°C, and a water hardness of 7.5 mg $CaCO_3$/L, had a 20-d LC_{50} between 242 and 261 mg F^-/L (Neuhold and Sigler 1960). In contrast, brown trout fry just having finished feeding on their yolk sac showed 50% mortality after about 90-h exposure to 20 mg F^-/L (Wright 1977). The water hardness was 73 mg $CaCO_3$/L. As fry develop into fingerlings, sensitivity decreases. For example, 72- and 96-h LC_{50} are 138.5 and 107.5 mg F^-/L, for fingerlings (aged two months) of rainbow trout and are 223.0 and 164.5 mg F^-/L, respectively, for fingerlings of brown trout (Camargo 1991a). In another study dealing with two month old fingerlings, Camargo and Tarazona (1991) reported 192-h LC_{50} values of 64 mg F^-/L for rainbow trout and 97.5 mg F^-/L for brown trout. For fingerlings of brown trout, the 48-h LC_{50} was estimated at 125 mg F^-/L (Woodiwiss and Fretwell 1974).

For rainbow trout averaging 5.8 cm in length, Pimentel and Bulkley (1983) recorded a 96-h LC_{50} of 51 mg F^-/L (soft water, 17 mg $CaCO_3$/L). The 96-h LC_{50} rose to 193 mg F^-/L as water hardness increased to 385 mg $CaCO_3$/L. When exposed to inorganic fluorides for a long term, fish can be more sensitive than fry. A 21-d LC_{50} of 8.5 mg F^-/L for yearling rainbow trout (averaging 10 cm in length) in soft water (hardness 12 mg $CaCO_3$/L) was reported by Herbert and Shurben (1964). A 20-d LC_{50} of 2.7 to 4.7 mg F^-/L for rainbow trout of 10-20 cm in length was obtained by Neuhold and Sigler (1960). Their experimental design included a static test with renewal, ambient temperature of 13°C, and a water hardness of <7.5 mg $CaCO_3$/L. In contrast to salmonid species, carp, 10.2 - 35.6 cm in length were found to be less sensitive having a LC_{50} of 75 to 91 mg F^-/L when tested at a temperature of 18.3 to 24°C and hardness of <7.5 mg $CaCO_3$/L (Neuhold and Sigler 1960)[1]. Adult mosquito fish (*Gambusia affinis*) are the most tolerant to acute exposure to inorganic fluorides of all fish species examined with a 24-h LC_{50} of 561 mg F^-/L (Wallen et al. 1957).

Growth and weight may be affected significantly by inorganic fluorides. Some species of freshwater fish like climbing perch (*Anabas testudineus*), snakehead (*Channa punctatus*), walking catfish (*Clarias batrachus*), catfish (*Heteropneustes fossilis*), and clown featherback (*Chitala ornata*) showed a mean reduction of 80% in growth and a

[1] Exposure time not specified but likely 20-d as for rainbow trout in the same study

mean reduction of 68% in weight when exposed to inorganic fluorides over a range from 6.9 to 52.5 mg F^-/L in a captive pond. The fluctuation in fluoride concentrations was due to seasonal conditions (Samal 1994). In comparison, fish in the unpolluted control pond developed normally.

Fluorides in water affects the behaviour of aquatic organisms. For example, the passage of salmon (*Oncorhynchus* spp.) during spring migration (1979-1980) through a fish-way adjacent to John Day hydroelectric dam on the Colorado River (Washington State) and downstream of an aluminium plant took nearly a week whereas passage at dams further downstream took only 1 to 2 days (Damkaer and Dey 1989). Effluents from the aluminium plant caused the elevated fluoride levels in the river water, but aluminium levels, which might have augmented fluoride toxicity, were not reported (Section 7.1.). In subsequent years, the aluminium plant reduced its fluoride discharge into the river. Fluoride levels in the river decreased from 0.3 - 0.5 mg F^-/L in 1982 to 0.1 - 0.2 mg F^-/L in 1984/85. The median passage time for spring chinook salmon (*O. tschawytscha*) at the John Day dam was slightly less than 48 h in 1984 and 28 h in 1985 (Damkaer and Dey 1989). Moreover, the percentage of chinook salmon "unaccountably lost" declined from 55% in 1980-82 to 5% in 1985. In complementary bioassays, chinook salmon, coho salmon (*O. kisutch*), and chum salmon (*O. keta*), exposed to water containing 0.5 mg F^-/L, had trouble swimming up an experimental fish-way. The authors found that 48% of the chinook, 36% of the coho salmon, and 22% of the chum salmon failed to choose a flume route and move upstream within 60 minutes. Fifty-three percent of the chinook salmon and 33% of the coho salmon failed to make a choice under exposure to 0.2 mg F^-/L. These percentages were significantly greater than those for the control group where 1 fish out of 119 tested failed to move up the flume. A threshold for fluoride sensitivity for chinook and coho salmon was estimated at 0.2 mg F^-/L (Damkaer and Dey 1989). Similarly, Foulkes and Anderson (1994) reviewed the behaviour of salmon species in the presence of high fluoride levels in freshwater and concluded that fluoride concentrations above 0.2 mg F^-/L have lethal effects on and inhibit the migration of salmon species. They predicted also that artificial fluoridation of drinking water causes higher fluoride levels than 0.2 mg F^-/L in freshwater in British Columbia (Nechako and Fraser River), and Washington (Snake and Columbia River).

An ecotoxicological analysis of the influence of an industrial effluent on fish and invertebrate populations in a regulated stream was conducted by Camargo (1992). Decreases in the fish population density and the complete disappearance of salmonid species (rainbow trout and brown trout) occurred at fluoride levels higher than 1.3 mg F^-/L. These effects, however, were probably due to low oxygen levels, with elevated fluoride concentration being a secondary factor.

7.3 Toxicity to Freshwater Amphibians

There are few data available on fluoride toxicity to amphibians. Thirty-five per cent (6 of 17) of leopard frogs (*Rana pipiens*) died within a 30-d exposure period to 150 mg F^-/L at a water hardness of 12 mg $CaCO_3$/L (Kaplan et al. 1964). At 200 mg F^-/L, 63% (12 of 19) of the frogs died. Embryonic and developmental life stages of leopard frogs were affected by levels as low as 1.0 mg F^-/L in distilled water, whereas the same adverse effects in pond water could only be observed at fluoride levels of 30 mg F^-/L (Cameron 1940). Kuusisto and Talkkä (1961) found adverse developmental effects in the metamorphosis and histological activity of the lymphoid glands in the common frog (*R.*

temporaria) at the exposure levels of to 1, 2, and 10 mg F^-/L; water hardness was not reported.

Mishra and Mohapatra (1998) examined haematological characteristics in toads (*Bufo melanostictus*) sampled from a site in India contaminated with fluorides. A decrease in haemoglobin content and total RBCs were found. The authors reported a relative weight loss of 14.6% in males and 15.7% in females at the contaminated site, compared to those from the control site (14.6% in males and 15.7% in females).

In a field study, Letnic and Fox (1998) investigated the impact of fluoride fallout on frog succession in Australia. In areas of high fluoride levels (ranging between 95 and 247 mg F^-/L) and low vegetation cover, low population abundance and succession of four species of *Myobatrachidae* spp. was observed; therefore, understorey vegetation density appears to positively affect frog succession. Fluoride pollution from an aluminium smelter caused damage in the vegetative cover and decreases in the canopy.

7.4 Toxicity to Freshwater Invertebrates

Although there is less information available on fluoride toxicity to invertebrates than fluoride toxicity to fish, invertebrates appear to be almost as sensitive under certain conditions. Commonly observed effects include death, impaired reproduction, and reduced growth. Some aquatic invertebrates may even be more sensitive than aquatic vertebrates.

Cytotoxicity of inorganic fluorides was investigated by Lilius et al. (1994). The authors found that freshly isolated rainbow trout hepatocytes were less sensitive to sodium fluoride than waterfleas (*Daphnia magna*). The 24-h EC_{50} for sodium fluoride was 140 mg F^-/L for immobilisation of *D. magna* and the 3-h EC_{50} for rubidium leakage of hepatocytes was 390 mg F^-/L. *Daphnia* tests were conducted at 21°C, and pH 7.6. Other variables, including concentration range and water hardness were not reported. Calleja et al. (1994) reported comparative acute toxicity *in vitro* cytotoxicity for aquatic invertebrates. The toxicity tests included Streptoxkit F with *Streptocephalus proboscideus,* Rotoxkit F with *Brachionus calciflorus*, and a test using *Daphnia magna*. The LC_{50}s for sodium fluoride were 70 mg F^-/L in the Streptoxkit F test, 290 mg F^-/L in the *Daphnia magna* test, and 180 mg F^-/L in the Rotoxkit F test.

Dave (1984) reported a 24-h EC_{50} of 205 mg F^-/L and a 48-h EC_{50} of 98 mg F^-/L for immobilisation of *D. magna* (water hardness of 250 mg $CaCO_3$/L). A similar result was obtained by Kühn et al. (1989) who reported a 24-h EC_{50} for immobilisation of 231 mg F^-/L for *D. magna*. Fieser et al. (1986) reported a 48-h LC_{50} of 180 mg F^-/L in *D. magna* (water hardness of 169.3 mg $CaCO_3$/L). In a laboratory bioassay, *Daphnia pulex* and *Simocephalus serrulatus* subjected to cryolite (Na_3AlF_6) in soft water had 48-h EC_{50} values for immobilisation of 2.71 and 5.43 mg F^-/L, respectively (Sanders and Cope 1966). In another study, relatively high EC_{50}s for immobilisation in four New Zealand cladoceran species and *D. magna* have been reported (Hickey 1989). The author found EC_{50}s for *D. magna*, *D. carinata*, *S. vetulus*, *Ceriodaphnia dubia*, and *Ceriodaphnia cf. pulchella* of 353.6, 353.6, 201.5, 157.9, and 83.2 mg F^-/L, respectively. Chronic toxicity tests (14-d) resulted in a LOEC >50 mg F^-/L for *D. magna* and *D. carinata*.

Camargo and co-workers exposed eight trichopteran species (net-spinning caddisflies) to inorganic fluoride in static bioassays under various exposure times. Water quality

conditions were similar among tests (*e.g.*, water hardness varied from 12 to 40 mg $CaCO_3$/L). For all species, as exposure time increased from 48-h to up to 144-h, LC_{50} values decreased. The most sensitive of their test species is *Hydropsyche bronta* with 48-, 96-, and 144-h LC_{50}s of 52.6, 17.0, 11.5 mg F^-/L, respectively (Camargo et al. 1992). Camargo (1996) re-evaluated these data and reported a slightly lower 96-h LC_{50} of 15.8 mg F^-/L. *H. occidentalis* and *Cheumatopsyche pettiti* experienced 96-h LC_{50}s of 34 and 42.5 mg F^-/L (Camargo 1996). Sub-lethal effects were also tested in five of the eight species. The 96-h EC_{50}s for net larvae migration ranged from 22.95 mg F^-/L for *H. bulbifera* to 43.09 mg F^-/L for *H. lobata*; *H. bronta* was not tested (Camargo and Tarazona 1990; Camargo and La Point 1995).

Long-term exposure to inorganic fluorides inhibits growth and reproduction in invertebrates, although an initial stimulatory effect may occur at low levels. A complex pattern of reproductive stimulation and inhibition was observed in *D. magna* exposed to one of twenty concentrations between 0 and 118.6 mg F^-/L in reconstituted hard water (250 mg $CaCO_3$/L) (Dave 1984). Stimulatory effects after 14-d exposure occurred at concentrations up to 0.0036, and after 21-d exposure at concentrations up to 0.007 mg F^-/L compared to controls. At levels of 14.8 mg F^-/L and above, inhibition was almost complete at both 14 and 21-d. The author suggested that at subinhibatory concentrations a combination of essentiality and hormesis may stimulate reproduction. The essential requirement for *D. magna* was estimated to be 0.004 mg F^-/L. No-observable-effect levels (NOELs) for both growth and parthenogenetic reproduction were estimated to be between 3.7 and 7.4 mg F^-/L. In comparison, a 21-d NOEL for reproduction of 14 mg F^-/L for daphnids was reported by Kühn et al. (1989). Fieser et al. (1986) exposed *D. magna* to one of six concentrations of NaF for three weeks in medium-hard water (101.6-181.3 mg $CaCO_3$/L) at 20°C. Egg production was stimulated relative to controls at concentrations up to 65 mg F^-/L. This increase, however, was offset by a reduction in live neonate production. The end result was a dose dependent decrease in hatchability rate (number of live neonates/number of eggs). Hatchability rate decreased sharply (39% of control) at 35.5 mg F^-/L and no live neonates were produced at the two highest doses (83.8 mg F^-/L and 141.6 mg F^-/L).

The exposure of fingernail clams (*Musculium transversum*) to 2.8 mg F^-/L during an eight week bioassay led to 60% mortality. Mortality among control clams (0.12 mg F^-/L) was also relatively high at 25% (Sparks et al. 1983). Tests were conducted at 20.9°C and pH 7.8. Water hardness was not reported but ranged from 341 to 374 mg $CaCO_3$/L in a similar test with lead nitrate. A concentration of 0.75 mg F^-/L in solution caused a reduction of approximately 50% of the ciliary activity in isolated clam gills; 1 mg F^-/L caused a ciliary arrest (no ciliary activity). In contrast, concentrations of cadmium chloride and lead nitrate did not appear toxic to fingernail clams (Sparks et al. 1983). Mane et al. (1987) examined the toxicity of inorganic fluorides to freshwater mussels (*Indonaia caeruleus*). The animals were exposed to 0.5, 2, and 5 mg F^-/L for 12-h. In a similar second experiment, the mussels were maintained in clean water following the 12-h exposure period. There were no consistent dose-dependent relationships between fluoride concentration and protein, glycogen and lipid content of various tissues. Mussels exposed to 0.5 mg F^-/L for 12-h and then clean water for 12-h had increased protein levels in the foot and hepatopancreas, decreased glycogen levels in the gill and gonad, and decreased lipid levels in the gonad. A dose dependant decrease in heart rate was observed after the 12-h exposure period, but not after the 12-h depuration period (Mane et al. 1987).

The relationship between population density of aquatic insects and fluoride contamination of a captive pond (polluted) was compared to a control pond (unpolluted) (Samal et al. 1990). Insects present included dragonflies, damselflies, bloodworms, diving beetles, water scorpions, caddisflies, and giant water bugs *Belostoma spp.* Samal et al. (1990) found that a seasonal fluctuation of fluoride levels in pond water was inversely proportional to the fluctuation in abundance of these aquatic insects in the polluted pond. The months August until January (*i.e.*, dry season) showed the highest fluoride levels (mean 31.02 mg F^-/L) and lowest insect abundance, whereas during the rest of the year, lower fluoride levels (mean 4.22 mg F^-/L) and higher abundance of these insects is found. When comparing the abundance of these aquatic insects in the captive pond verses the control pond, the monthly average number for dragonflies, bloodworms, diving beetles, and caddisflies was higher (61.8%, 81.1%, 75.7%, and 51.1%, respectively) at the captive pond site, whereas the average number of damselflies and water scorpions was higher (83% and 68.4%, respectively) at the control pond site. The average number of giant water bugs did not significantly differ between the two sites (15% higher at the captive pond).

7.5 Toxicity to Freshwater Plants

Adverse effects observed in aquatic plants exposed to inorganic fluorides include mortality, growth inhibition and enzyme inhibition, especially in the presence of aluminium (Smith and Woodson 1965; Groth 1975a;b; Hekman et al. 1984; Shirke and Chandra 1991; Nichol et al. 1987; Husaini et al. 1996; Rai et al. 1998). In some cases, low levels may stimulate growth (Joy and Balakrishnan 1990). Samecka-Cymerman and Kempers (1990) tested the toxicity of inorganic fluorides to nine populations of liverwort (*Scapania undulata*). At doses of 100 mg F^-/L and greater, the length gametophytes, and the length and number of lateral branches decreased with increasing concentration. Below 100 mg F^-/L, growth was inhibited in some populations but stimulated in others. Five of the populations had a LC_{100} of 450 mg F^-/L, while four were slightly more sensitive with a LC_{50} of 400 mg F^-/L. At 250 mg F^-/L, all plants, except those from one population survived.

Joy and Balakrishnan (1990) studied the effect of fluorides on axenic cultures of diatoms and subjected *Nitzschia palea*, a freshwater diatom, to fluoride concentrations from 10 to 110 mg F^-/L. The diatom was tolerant to higher fluoride concentrations and growth (in terms of cell numbers and chlorophyll content) was stimulated.

The green alga, *Chlorella pyrendoidosa*, is the most sensitive plant and shows a growth inhibition of 37% after 48-h exposure to fluoride levels as low as 2.0 mg F^-/L (Smith and Woodson 1965). A complete inhibition of photosynthesis occurred in *Synechococcus leopoliensis* at 20 mg F^-/L (pH 6.16) and at 50 mg F^-/L (pH 6.68; Nichol et al. 1987). Hekman et al. (1984) reported a 13% decrease in doubling rate and a one hour lag in growth for the same species exposed to 25 mg F^-/L. At 50 and 150 mg F^-/L, the lags in growth were 18.5 and 76-h, respectively. Other freshwater planktonic algae *Oscillatoria limnetica*, *Ankistrodesmus braunii*, *Scenedesmus quadricauda*, *Cyclotella meneghiniana*, and *Stephanodiscus minutus* did not experience reductions in growth at 50 mg F^-/L (Hekman et al. 1984). The protist, *Chlamydomonas reinhardtii*, exposed to 0.95 mg F^-/L did not experience any changes in growth (Joseph et al. 1995).

The effects of fluorides on soluble protein in duckweed (*Spirodela polyrrhiza*) in field and laboratory experiments have been investigated by Shirke and Chandra (1991). A

significant reduction (*i.e.*, 10.5%) of soluble protein in duck-weed (*S. polyrrhyza*) was reported at 25 mg F^-/L after 24-h exposure; given the same concentration of sodium fluoride, a reduction of 34.7% was recorded after 360-h exposure.

7.6 Toxicity to Marine Fish

Limited data are available on the toxic effects of fluorides on marine fish. A series of mesocosm studies was conducted by Hemens and Warwick (1972) and Hemen et al. (1975). Artificial communities containing fish, invertebrates, plants and algae were established and given ample time to stabilise before experiments began. In each mesocosm, sodium fluoride was periodically added to maintain constant test conditions. Exposure to sodium fluoride was 68 to 113 days. Juvenile mullet (*Mugil cephalus*) exposed to 5.88 mg F^-/L for 68 days showed 10% mortality and reduced growth for fish 16-18 mm in length (Hemens et al. 1975). Juvenile mullet exposed to 5.65 and 5.70 mg F^-/L for 113 days experienced 18.2 and 13.6% mortality rate, respectively (Hemens et al. 1975). Thirty percent mortality was observed in juvenile mullet exposed to 52 mg F^-/L for 72 days (Hemens and Warwick 1972). The control group (1.05 mg F^-/L) experienced 30% mortality as well; but, 66% of the deaths were accidental in that fish jumped from the tank. The animals exposed to 52 mg F^-/L were in poor physical condition, whereas those from the control group who survived were active and in good physical condition (Hemens and Warwick 1972). In laboratory tests, mullet experienced no-observable-adverse-effects when exposed to fluoride concentrations up to 100 mg F^-/L for 96-h (Hemens and Warwick 1972).

7.7 Toxicity to Marine Invertebrates

The larvae of brine shrimp (*Artemia salina*) are the most sensitive marine invertebrate of those tested. During a 12-d static renewal test, a significant reduction in growth of about 18.5% was observed at 5.0 mg F^-/L (Pankhurst et al. 1980). Using *in vitro* cytotoxicity tests, Calleja et al. (1994) reported marine toxicity tests including Artoxkit M with *Artemia salina*, and Microtox™ using *Photobacterium phosphoreum*. The LC_{50}s for sodium fluoride were 12 008 mg F^-/L in the Microtox™ test and 3 040 mg F^-/L in the Artoxkit M test.

Three of four blue mussels exposed to 10 mg F^-/L for 30 days died. And, the fourth died on day 36 (Wright and Davison 1975). In a study of fluoride discharges from an aluminium smelter in South Africa, Hemens and Warwick (1972) found that 50% of brown mussels (*Perna perna*) died after exposure to 7.2 mg F^-/L for 20 days; at 83.4 mg F^-/L all mussels died within 5 days. As these mussels were not fed during the experiment, starvation likely placed additional stress on these animals. Mortality was observed in an unspecified species of oyster exposed to 10 mg F^-/L for 30 days (Moore 1969).

Moore (1971) found a growth decrease of 4.5% per moult cycle, with an accumulative effect over a 20 moult life cycle. This resulted in a growth reduction of 52% for blue crab (*Callinectes sapidus*) exposed to 20 mg F^-/L, compared to the controls. Connell and Miller (1984) reviewed toxicity data for several marine invertebrates. They reported an LC_{100} for oysters (*Crassostrea virginica*) exposed to 32 mg F^-/L for 60 days, and an LC_{45} for shrimp (*Palaemon pacificus*) exposed to 52 mg F^-/L for 72 days. In mesocosm studies, crab (*Tylodisplax blephariskios*) and shrimp (*Palaemon pacificus*) subjected to

52 mg F⁻/L for 72 days showed 70.7 and 45.5% mortality, respectively (Hemens and Warwick 1972).

Connell and Airey (1982) conducted a chronic study on the estuarine amphipods *Grandidierella lutosa* and *Grandidierella lignorum*. The experiments were multi-generational and were carried out over 90 days. In the first experiment, the amphipods were exposed to sodium fluoride at levels between 1.50 and 9.22 mg F⁻/L. Exposure to 6.90 mg F⁻/L caused a significant reduction in population growth rate and survival. In the second experiment, the amphipods were exposed to levels between 1.34 and 6.39 mg F⁻/L. Exposure to 6.08 mg F⁻/L caused a significant reduction in growth rate and survival.

7.8 Toxicity to Marine Plants

Marine plant species are stimulated by fluoride levels that are toxic to other organisms. These results are similar to those obtained for some freshwater plants. For example, growth of the marine phytoplankton (*Rhodomonas lens*) is stimulated 20 to 30% above that of the control at concentrations between 10 and 100 mg F⁻/L (Oliveira et al. 1978), whereas fish and invertebrates may die at this level.

Relatively high levels of inorganic fluorides are needed to elicit toxic effects in marine plants. Antia and Klut (1981) observed the reaction of the dinoflagellate (*Amphidinium carteri*) and the algal species, *Pavlova lutheri*, when exposed to sodium fluoride. *A. carteri* showed a 20% reduction in growth rate at 150 mg F⁻/L and a 95% reduction at 200 mg F⁻/L. *P. lutheri* also showed a 48% reduction in growth rate at 150 mg F⁻/L. Green alga (*Dunaliella tertiolecta*) and the diatom (*Thalassiosira weissflogii*) showed only slight decreases in growth-rate and maximum growth density, whereas the diatom (*Chaetoceros gracilis*) had stimulated growth rates (Antia and Klut 1981). When the cultures were transferred to uncontaminated media, normal growth resumed. After two cycles of exposure and decontamination, *A. carteri* adapted to 200 mg F⁻/L and was able to grow to 86% of the control rate (Antia and Klut 1981). Joy and Balakrishnan (1990) studied stimulation in growth by exposing a brackish water diatom, *Amphora coffeaeformis*, to fluoride concentrations ranging from 10 to 110 mg F⁻/L. Results indicated *A. coffeaeformis* tolerated high fluoride concentrations up to 110 mg F⁻/L without adverse effects. Growth stimulation in terms of cell numbers and chlorophyll was recorded at 70 mg F⁻/L, but at 90 mg F⁻/L a decline in growth occurred. The adaptive ability of some plant species to fluoride suggests that the tolerance is gene based and inherent.

7.9 Toxicity to Semi-Aquatic Animals (Mammals and Birds)

Responses of herring gulls (*Larus argentatus*) and common gulls (*Larus canus*) to exposure to inorganic fluorides were investigated by Vikøren and Stuve (1996). The authors examined eggs of both species from breeding colonies (Karmøy and Sunndal) exposed to fluoride emissions, and from reference sites (*i.e.*, no fluoride outputs) in Norway. Although a positive correlation of fluoride concentration in femurs of breeding female birds and in the shell of their eggs could be identified, differences in egg volume, shell thickness, percent fertilised eggs, and changes in the morphology of bones (due to high fluoride levels in gull bones) could not be found Vikøren and Stuve (1996).

Culik (1987) researched fluoride concentrations in adélie penguins (*Pygoscelis adeliae*) and other bird species during Antarctic expeditions in 1980-81 and 1984-85. Mean fluoride concentrations in femurs were 9.60 mg F^-/g dw (compacta) and 2.32 mg F^-/g dw (spongiosa). In preliminary experiments, adélie penguins were fed 200 mg F^-/d and after 14 days of exposure some animals experienced significant weight loss while 75% of the animals were dead. In later experiments a tolerance to these high fluoride levels is reported as a result of adding calcium to the diet. When feeding on krill in nature, penguins are subjected to high fluoride levels (*e.g.*, 240 mg F^-/d) which they tolerate without ill effects. This tolerance occurs because fluoride exists in the cuticle of krill which penguins are unable to digest as they have no caeca which possibly enables the digestion of chitin found in the cuticle (Culik 1987).

8. WATER QUALITY GUIDELINES

8.1 Recreational Water Quality and Aesthetics

There was no evidence to indicate that recreational water quality and aesthetics would be impaired by inorganic fluorides under current regulations and conditions of use and disposal (Warrington 1990; Health and Welfare Canada 1992). Health and Welfare Canada (1992) did not report a guideline for Canadian Recreational Water Quality; therefore, water quality guidelines for this water use are not recommended at this time.

8.1.1 Summary of Existing Guidelines

No Canadian or U.S. water quality criteria, guidelines, objectives or standards were found for inorganic fluorides specific to recreation and aesthetics (Warrington 1990; Health and Welfare Canada 1992).

8.2 Aquatic Life

Inorganic fluorides at low concentrations in the aquatic environment can elicit slight effects that are statistically significant and ecologically relevant. Sensitive characteristics for fish include survival, growth, reproduction, and behavioural endpoints.

To develop water quality guidelines for aquatic life, scientific literature dealing with acute and chronic toxicity data were thoroughly evaluated for their usefulness for guideline derivation. Studies were ranked as primary, secondary, or ancillary as per criteria outlined by CCME (1991; 1999). Typically only primary studies are considered in the fulfilment of the minimum data set requirements for guideline derivation. Some high quality studies were ranked secondary, owing to static test conditions (Appendices B1; B2). In contrast to volatile substances, fluoride concentration is not expected to change significantly in static tests; therefore, these studies were considered for guideline development. Studies ranked secondary for other reasons (*e.g.*, concentration not measured, hardness not reported) were not considered for guideline development. In addition, studies conducted under conditions (*e.g.*, hardness, temperature; see section 7.1) or that used species not found in North America were also not considered.

According to the data requirements (minimum two acute and/or chronic studies for fish), an interim guideline for inorganic fluorides in freshwater could be developed using one study with cold-water fish species and a minimum of two acute and/or chronic studies for invertebrates from different classes, one planktonic species resident in North America. A full guideline could not be derived for inorganic fluorides because there was insufficient information (8.2.1. Freshwater Guideline Derivation, Data Gaps) according to protocol requirements. No guideline for marine waters was developed because neither full nor interim data requirements were satisfied.

8.2.1 Freshwater Guideline Derivation

Key studies for freshwater life predominantly focused on survival. Primary toxicity studies on freshwater life include, for example, Pimentel and Bulkley (1983) who recorded a 96-h LC_{50} of 51.0 mg F/L at 17 mg $CaCO_3$/L for rainbow trout averaging 58 mm in length. These authors demonstrated a linear relationship between water toxicity and hardness. Brown trout (*Salmo trutta*) fry exposed to 20 mg F/L experienced 50%

mortality in 90 hours (73 mg $CaCO_3$/L) (Wright 1977). Fingerlings of rainbow trout and brown trout experienced a 192-h LC_{50} at inorganic fluoride levels of 64.1 and 97.5 mg F^-/L, respectively, when tested at 21 mg $CaCO_3$/L (Camargo and Tarazona 1991). In primary acute and chronic toxicity studies by Fieser et al. (1986), neonates of *Daphnia magna* experienced impaired reproduction and reduced hatchability at fluoride levels of 34 mg F^-/L beginning on day 12 of a 21-d exposure test. A series of high quality secondary bioassays on eight species of net-spinning caddisflies by Camargo (1996), Camargo et al. (1992), Camargo and Tarazona (1990) among others were considered for guideline derivation. *Hydropsyche bronta* was the most sensitive species with 48-, 96-, and 144-h LC_{50}s of 52.6, 17.0, and 11.5 mg F^-/L, respectively (Camargo et al. 1992). Camargo (1996) re-evaluated some of these data and reported a slightly lower 96-h LC_{50} of 15.8 mg F^-/L. Sub-lethal effects were also tested in five of the eight species. The 96-h EC_{50}s for net larvae migration ranged from 22.95 mg F^-/L for *H. bulbifera* to 43.09 mg F^-/L for *H. lobata*; *H. bronta* was not tested (Camargo and Tarazona 1990; Camargo and La Point 1995). Water quality conditions were similar among tests (*e.g.*, water hardness varied from 12 to 40 mg $CaCO_3$/L).

Secondary toxicity studies not considered for guideline derivation still provide supporting evidence. Neuhold and Sigler (1960) estimated the 20-d LC_{50} values to be between 2.7 and 4.7 mg F^-/L for rainbow trout (*Oncorhynchus mykiss*), and between 75 and 91 mg F^-/L for carp (*Cyprinus carpio*). In this study, water temperature was 13°C and hardness was very soft (<7.5 mg $CaCO_3$/L). A 10-d LC_{50} between 2.3 and 7.3 mg F^-/L in soft water was obtained by exposing juveniles of rainbow trout to sodium fluoride (Angelovic et al. 1961). This study was not used because water was artificially softened to an unspecified calcium concentration and temperature was not reported. Herbert and Shurben (1964) reported a 21-d LC_{50} of 8.5 mg F^-/L for yearling rainbow trout in soft (12 mg $CaCO_3$/L) lake water. There were no replicates in this study and concentrations of F^- were not measured.

Field and laboratory studies demonstrating the neurotoxic effects of fluorides provides supporting evidence (Damkaer and Dey 1989). Migration patterns of chinook (*O. tschawytscha*), chum (*O. keta*), and coho (*O. kisutch*) salmon were disrupted when fish were exposed to an inorganic fluoride level of 0.5 mg F^-/L prior to and during migration runs. For these species, the authors suggest a threshold for fluoride sensitivity of 0.2 mg F^-/L (Damkaer and Dey 1989). The field part of this study could not be used for guideline derivation primarily because elevated aluminium levels in the river may have been a confounding factor. Also, fluoride levels and water quality data were not reported for all years of the study. The results from the experimental fish-way tests are not suitable for guideline derivation because water quality data were not reported. Notwithstanding, site-specific objectives may require consideration of salmon migration (see section below).

With regard to invertebrates, Dave (1984) estimated the 21-d NOEL for growth and reproduction in *Daphnia magna* to be between 3.7 and 7.4 mg F^-/L in reconstituted hard water (250 mg $CaCO_3$/L); however, there was no clear dose-response relationship. Sanders and Cope (1966) investigated survival of *D. pulex* and *Simocephalus serrulatus*. The 48-h EC_{50} for immobilisation of *D. pulex* and *S. serrulatus* were 2.71 and 5.43 mg F^-/L, respectively. This study was not selected for guideline development because the authors used cryolite (Na_3AlF_6) as a test substance. Because cryolite contains Al, Al-based toxicity could be a confounding factor to the results of this study. The exposure of fingernail clams (*Musculium transversum*) to 2.8 mg F^-/L during an

eight week bioassay led to 60% mortality (Sparks et al. 1983). This study was not selected because of high mortality (25%) among control clams.

Most plant species were not as sensitive as fish and invertebrate species, with one exception. The green alga, *Chlorella pyrendoidosa*, showed a growth inhibition of 37% after 48-h exposure to fluoride levels as low as 2.0 mg F^-/L (Smith and Woodson 1965). The species was tested at 26°C, pH 6.8 in Knop's medium. The age of this study is of concern in guideline derivation; nevertheless it is supportive.

8.2.2 Recommended Freshwater Guideline

The critical study used for guideline development was reported in both Camargo et al. (1992) and Camargo (1996). In this acute, static toxicity study, the caddisfly *Hydropsyche bronta* experienced 48-, 96-, and 144-h LC_{50}s of 52.6, 15.8, 11.5 mg F^-/L, respectively. Sodium fluoride was used as the fluoride-containing compound. Duplicate tests were conducted with a control and five different fluoride concentrations. Throughout the experiment, fluoride concentrations and physicochemical parameters were measured. The water quality conditions (temperature of 18°C; pH 7.8, 9.5 mg/L for dissolved oxygen; water hardness of 40.2 mg $CaCO_3$/L) are suitable for *H. bronta* and applicable to Canadian fresh waters. Moreover, *Hydropsyche bronta* is a caddisfly species found in Canada

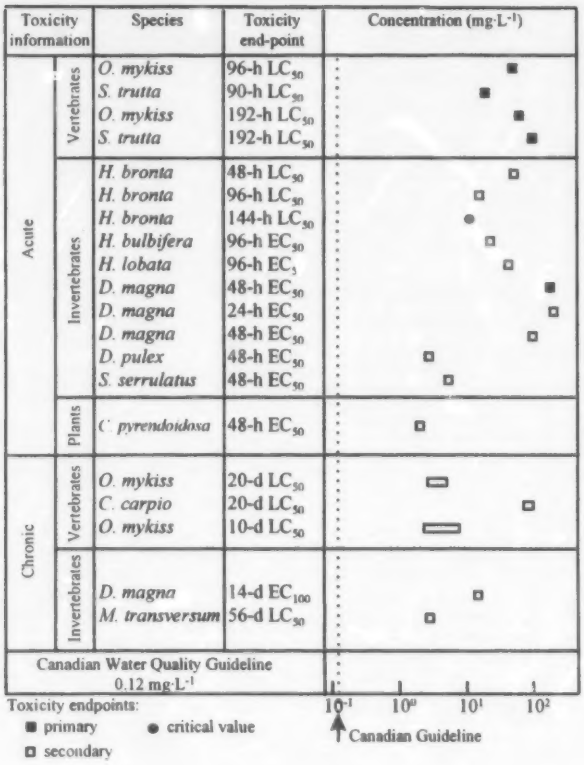

Figure 1. Select freshwater toxicity data for inorganic fluorides.

The interim guideline for total inorganic fluorides is 0.12 mg F⁻/L. This guideline is derived from the lowest acceptable adverse effect level reported: a 144-h LC_{50} value of 11.5 mg F⁻/L for the caddisfly *Hydropsyche bronta* (Camargo et al. 1992). As this value is an acute, lethal endpoint, a safety factor of 0.01 was applied.

Several studies have shown that inorganic fluoride toxicity is negatively correlated with water hardness and positively correlated with ambient temperature (Angelovic et al. 1961, Pimentel and Bulkley 1983; Smith et al. 1985; Fieser et al. 1986), however, insufficient data currently exists to develop a quantitative correlation or a guideline matrix. Nevertheless, it is expected that factors such as water hardness and temperature, presence of cations such as calcium, magnesium (Pimentel and Bulkley 1983; Smith et al. 1985), and, potentially, selenium (Pang et al 1996), or anions such as chloride (Neuhold and Sigler 1962) can reduce the toxicity of inorganic fluorides on a site-specific basis. At such sites, therefore, environmental concentrations may exceed the guideline value for the protection of aquatic life without necessarily leading to noticeable negative effects. Notwithstanding, fluoride toxicity to aquatic plants (Husaini et al. 1996; Rai et al. 1998) and, potentially, aquatic animals is enhanced by the presence of metals, especially aluminium. Therefore, judiciousness is required when using guidelines at a specific site. Further multifunctional experiments at various combinations in the parameters (*i.e.*, water hardness and temperature) are needed to derive Canadian water quality guidelines which are based on these parameters.

In the development of site-specific objectives, impacts of inorganic fluorides, especially in combination with aluminium on the migratory capabilities of anadromous fish should be considered where appropriate anadromous fish species are more sensitive to inorganic fluorides in fresh waters (effects observed at levels as low as 0.5 mg F⁻/L; Damkaer and Dey 1989) than in marine waters where the natural ambient concentration inorganic fluoride is about 1.3 mg F⁻/L (Dave 1984; Foulkes and Anderson 1994).

8.2.3 Data Gaps

There is sufficient information available to establish an interim freshwater guideline for aquatic life. The available data set for toxicity studies contains six different fish species (including rainbow trout as a cold water fish), and six invertebrate species (three daphnids and three benthic invertebrates). There was difficulty finding literature representative of fluoride toxicity to aquatic freshwater plants (*e.g.*, F⁻ concentration in test solution was not measured by Nichol et al. (1987) while Shirke and Chandra (1991) used aquatic macrophytes as defluoridating agents to accumulate fluorides). Also, evaluating fluoride toxicity to aquatic plants is complex and many study species demonstrate a tolerance for high accumulation rates due to high exposure rates (Groth 1975a; Hekman et al. 1984).

To establish a full freshwater guideline, additional information from at least two chronic studies for fish (one cold water and one warm water species), one more chronic study on invertebrates (other than a daphnid), and one study on a freshwater vascular plant or freshwater algal species resident in North America, is required.

In addition to the outstanding data that are necessary to satisfy the requirements for a full guideline, future research should better define the water hardness and temperature based relationships as the toxicity of fluoride is dependent on these relationships. Due to limited data, scientifically valid water hardness and temperature relationships to toxicity

could not be calculated. Such relationships could contribute to the development of a guideline as well as site-specific objectives. Lastly, many of the high quality studies are not recent publications. It would strengthen the database in general if some of the older studies were repeated in modern laboratory facilities for the same and/or different species and life stages.

8.2.4 Summary of Existing Guidelines

British Columbia recommends that the total inorganic fluoride concentration should not exceed 0.2 mg F^-/L when the water hardness is less than 50 mg $CaCO_3$/L and 0.3 mg F^-/L when the water hardness is greater than 50 mg $CaCO_3$/L (Warrington 1996). Manitoba endorsed a tissue residue guideline for fluorides for the protection of aquatic life of 150.0 mg·F^-/kg. At present, there is no value referenced for the protection of aquatic life (Williamson 2000). Quebec uses two guideline values for inorganic fluorides: these include a value of 4.0 mg F^-/L (acute toxicity) and a value of 0.2 mg F^-/L (chronic toxicity) to protect aquatic life when water hardness is less than 120 mg F^-/L (MENVIQ 1999). In the Netherlands, fluoride concentrations in surface water should not exceed 1.5 mg F^-/L (VROM 1991; 1999). Germany derived a surface water guideline for fluorides of 0.7 mg F^-/L (MURL 1991). In addition to these jurisdictional guidelines, Pimentel and Bulkley (1983) recommended interim maximum chronic exposure levels which range from 2.5 mg F^-/L at a water hardness of 17 mg $CaCO_3$/L (*i.e.*, soft water) to 9.6 mg F^-/L at a hardness of 385 mg F^-/L (*i.e.*, hard water).

8.2.5 Marine Guideline Derivation

There are too few reports available on fluoride toxicity to marine biota to fulfil the data requirements for a marine guideline. Toxicity studies describing a range of effects such as growth reduction, impaired reproduction, and survival are available for invertebrates but not for marine fish (Parker 1986). Some information on bioaccumulation of inorganic fluorides in fish exists. Marine toxicity studies focused on invertebrates including shrimp, mussel, oyster, and crab. More detailed and high quality toxicity studies, especially on fish, but also on invertebrates, are required to establish a marine guideline. The provision of adequate food for invertebrates, such as mussels, was a consistent problem for long-term toxicity studies.

Some marine organisms appear to withstand unnaturally high fluoride levels without any ill effects (Wright and Davison 1975). Marine waters are naturally higher in fluoride levels (1.0 to 1.7 mg F^-/L) than in fresh waters (0.01 - 11.0 mg F^-/L). In toxicity test solutions with up to 30 mg F^-/L, only blue mussels (*Mytilus edulis*) experienced death at 10 mg F^-/L. The swimming crab (*Portunus depurator*), edible crab (*Cancer pagurus*) and shore crab (*Carcinus maenas*) did not show any adverse effects. This observation may be supported by Neuhold and Sigler (1962) who found that chlorides in water reduced the sensitivity of rainbow trout (*Oncorhynchus mykiss*) to inorganic fluorides. Marine waters contain higher levels of chlorides than fresh waters.

The following key studies contain important environmentally relevant effects. In a primary test, a LC_{75} for blue mussels (*Mytilus edulis*) exposed to 10 mg F^-/L for 30 days has been observed (Wright and Davison 1975). The following toxicity data are ranked secondary. The most sensitive invertebrates are larvae of brine shrimp (*Artemia salina*). A 12-d, secondary static test, caused a significant reduction in growth of 18.5% at 5.0 mg F^-/L (Pankhurst et al. 1980). The blue crab (*Callinectes sapidus R.*) showed a

4.5% reduction in growth per moult when exposed to 20 mg F/L (Moore 1971). In a review of toxicity data for several marine invertebrates, Connell and Miller (1984) found a 60-d LC_{100} for oysters (*Crassostrea virginica*) at 32 mg F/L, and a 72-d LC_{45} for shrimp (*Palaemon pacificus*), exposed to 52 mg F/L. Crab, *Tylodisplax blephariskios*, and shrimp, *P. pacificus*, exposed to 52 mg F/L for 72 days in a mesocosm, experienced 70.7 and 45.5% mortality, respectively (Hemens and Warwick 1972). Fifty percent of brown mussels (*Perna perna*) died after exposure to 7.2 mg F/L for 20 days (Hemens and Warwick 1972).

8.2.6 Recommended Marine Guideline

Due to paucity of acceptable toxicity data, no guideline for inorganic fluorides to protect marine life could be elaborated at present.

8.2.7 Data Gaps

Nine different species of invertebrates including shrimp, mussel, crab, and oyster were tested in the presented key studies. No toxicity studies on marine fish that meet the standards set forth in the protocol could be located.

Full marine guidelines require at least three additional toxicity studies on temperate marine fish, two of them chronic. Further, at least one study on a temperate vascular marine plant is needed.

To establish an interim marine life guideline at least two additional acute or chronic studies on two or more fish species (one must be a temperate species) are required.

8.2.8 Summary of Existing Guidelines

British Columbia proposes a limit of 1.5 mg F/L based on the calculation of intake levels for humans consuming marine food, fish and invertebrates (Warrington 1996). No other marine guidelines or criteria for inorganic fluorides were found.

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APPENDIX A: ANALYTICAL METHODS

Measurement of inorganic fluorides in environmental samples is restricted to detecting the free anion (F^-), limiting the ability to distinguish between different chemicals species. The most commonly used analytical method to measure the free anion is the fluoride ion-selective electrode (F-ISE) (Neumüller 1981; Harzdorf et al. 1986; ATSDR 1991). Modifications in the sample preparation and the instruments themselves can change the sensitivity and recovery, and therefore the detection limit. Typical detection limits of the F-ISE for inorganic fluorides range from 0.1 - 300 ng F^-/m_3 (air), 0.001 - 1.0 mg F^-/L (water), and 0.05 - 20 mg F^-/kg (organic tissues, wet weight). Other methods that may be used to measure the fluoride ion include colourimetry, ion chomatography, atom absorption spectroscopy and photon activation (Neumüller 1981; ATSDR 1991).

In the majority of cases some form of sample pre-treatment is necessary to free the complexed and masked inorganic fluorides, and to convert the matrix-bound fluorides into the free inorganic fluoride ion, and thus permit the measurement of the total fluorides content of the sample.

The Ion Selective Electrode (ISE) functions by means of a membrane which gives an electrochemical response proportional to the inorganic fluoride ion activity in the sample (WHO 1984). One of the chief problems associated with measuring inorganic fluorides with the ISE is that large deviations from linearity occur at low inorganic fluorides levels, which makes the results less reliable near the detection limit. Nevertheless, the ISE has been widely used for the analysis of inorganic fluorides in water, industrial effluents, air, aerosols, flue gases, soils, minerals, and plants (WHO 1984). Accurate measurement with the ISE requires that the electrode maintain a "steady state" for the duration of the measurement period. Cattrall et al. (1989) suggests that a steady state has been reached when the potential does not vary more than ±0.1 mV over a 5 minute period. The authors used a mathematical expression derived by Chek (1984) to fit the electrode response curve and compute the steady state potential. Cattrall et al. (1989) found this approach to be very useful when analysing plant samples having a low inorganic fluorides content. Other authors advocate the use of sample concentration to eliminate the problem of variations in the response curve of the electrode. Concentration of the sample has been shown to increase the sensitivity of the ISE by 1 to 2 orders of magnitude, enabling samples containing a few µg/L (*i.e.*, 0.01 - 0.1 µmol/L) to be measured accurately (Campbell 1987).

For analysis by the ISE, matrix-bound inorganic fluorides can be released by several different procedures which have varying degrees of success. Common procedures are ashing (burning the sample in an open or closed vessel, *e.g.*, oxygen flask, chamber, or bomb) or digesting (treatment of sample with strong inorganic acids or bases such as hydrochloric acid, nitric acid, or sodium hydroxide). There are three main problems associated with the open ashing of a sample: 1. volatilisation and hence loss of organofluorine compounds occurs at relatively low temperatures; 2. the sample can become contaminated with any extraneous inorganic fluorides present in the laboratory or equipment; and 3. volatilisation of inorganic fluorides occurs at temperatures exceeding 550°C (Campbell 1987). Despite these inherent disadvantages, many investigators continue to rely on the open ashing technique. In contrast, the use of the oxygen bomb for ashing (*i.e.*, a closed system) is not subject to the above errors, and when done properly, is considered to be the most accurate method, because only here all forms of non-ionic fluorine are converted into free inorganic fluoride ions (Campbell

1987; Singer and Ophaug 1983; Gustafsson and Njenga 1988). It releases the inorganic fluorides from inorganic complexes, breaks down any organic material which may contain inorganic fluorides, and releases any inorganic fluorides which may be physically trapped in the sample matrix. If ashing is not performed, neither organic nor non-friable inorganic fluorides will be determined, and the results will not reflect the true inorganic fluorides content of the sample. The inorganic fluorides content measured by the digesting method is referred to as acid- or alkali-labile inorganic fluorides, and is sometimes (erroneously) termed "total" inorganic fluorides to distinguish it from any free F^- present which can be titrated directly with the ISE. The use of alkaline digestion is advocated in cases where the sample may not be acid-labile (Harzdorf et al. 1986).

Following the ashing or digesting, the free inorganic fluoride has to be isolated (extracted) and often concentrated before it can be analysed quantitatively using the inorganic fluorides-sensitive ISE. The isolation and concentration is usually accomplished either by steam distillation or by micro-diffusion with hexamethyldisiloxan (HMDS) as trimethylflourosilane in Conway diffusion cells or modifications thereof (Venkateswarlu 1992; Gustafsson and Njenga 1988; Campbell 1987; Sager 1987; Singer and Ophaug 1983). The isolation step ensures that the inorganic fluorides formed during ashing and digestion is freed from contaminants which may react in a non-specific manner with the reagents used in colourimetric determinations, or interfere with the measurement of inorganic fluorides when using an ISE. The concentration step serves to bring the sample into the detection range of the method employed.

In the steam distillation method, the ashed sample is acidified in order to release the inorganic fluorides as the volatile HF, which is then distilled over. This method is time-consuming and only 2 to 3 samples per day can be processed, and is, therefore, not commonly used (Sager 1987). Furthermore, the procedure has to be performed carefully in order to avoid contamination of the sample. Volatilisation of other halogen acids and sulphides can be minimised by the addition of the silver salt of the acid used to liberate the hydrogen fluoride (Campbell 1987).

Using the micro-diffusion method, hydrofluoric acid is liberated from ashed or unashed samples using perchloric or sulphuric acid. Under acid conditions hexamethyldisiloxan (HMDS) dissociates to form the trimethylsilane radical which in turn reacts with inorganic fluoride ions in solution to form the volatile trimethylfluorosilane (TMFS). TMFS diffuses from the aqueous phase into the air and is then trapped in an inverted drop of NaOH on the lid of the diffusion chamber. Under basic conditions the trimethylfluorosilane reacts with the hydroxyl ion to form trimethylsilanol and the free inorganic fluoride ion. Interference from aluminium, iron and silica is minimised by the use of perchloric acid in preference to sulphuric acid. Diffusion is usually completed within 6 to 10 hours (bone, urine, serum, and water samples), but can take up to 48 hours (soft tissue, fluoroelastomer samples) (Venkateswarlu 1992).

Certain di- and trivalent free cations, *e.g.*, Al^{3+}, Mg^{2+}, can cause interference with the functioning of the ISE, and must, therefore, be bound, *i.e.*, chelated, prior to inorganic fluoride ion measurement. Common chelating agents are tri-ammonium citrate (TAC) or trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (DCTA). High levels of the OH^- ion , *i.e.*, high pH, can also lead to interference, while at low pH HF_2^- is formed, which also leads to erroneous measurements (Nicholson and Duff 1981). The pH and the total ionic strength of the sample must, therefore, be adjusted. This is achieved by the addition of Total Ionic Strength Adjustment Buffer (TISAB) solution, which maintains the

pH close to the optimum value of approximately 5.4, and minimises the interference caused by other ions by chelating with TAC or DCTA. Harzdorf et al. (1986) has recommended the use of citrate as the chelating agent since it provides optimum conditions in terms of response time and the masking of interfering ions, and maximises the electrode's lifetime. However, one of the main uncertainties associated with the analysis of inorganic fluorides using the ISE is that the chelating agent in the TISAB may not always bind or dissociate all of the interfering ions immediately. There is no general consensus on the time required for the buffer to chelate interfering ions, although most studies allow the sample to stand for at least 20 minutes before measurement. Nicholson and Duff (1981) reported that the results are significantly improved when the same sample is left for 24 hours, rather than 20 minutes, however, use of the longer time is often impractical and detracts from the main advantage of the ISE, which is its speed. Their study of eleven different buffering solutions showed that the most pronounced effect of the chelating agent occurred over the first 10 to 20 minutes following addition of the buffer. They concluded that 20 minutes was an acceptable and feasible alternative to the 24 hour delay. However, such short times may not be sufficient if the sample has an aluminium content which approaches or exceeds that of the inorganic fluorides, as may be the case in drinking water samples.

For use with solid samples such as silicates, bauxite, phosphates, soils, coal, and plant material, Sager (1987) has recommended Tiron (pyrocatechol-3,5-disulphonic acid, disodium salt) as a suitable complexing/buffering agent. Other authors have noted that although the analytical results obtained using Tiron show good sensitivity and reproducibility, the masking capacity of this chelator is too poor to warrant its general use (Nicholson and Duff 1981). Other analysts have suggested using either DCTA, mannitol, or 2-amino-2-hydroxymethyl-1,3-propanediol (TRIS) (Campbell 1987).

As with other stages of the analytical procedure, care must be taken to avoid loss of volatile inorganic fluorides or contamination with extraneous inorganic fluorides when using the ISE (Harzdorf et al. 1986). Also, buffer solutions should not be kept for more than two weeks, as their masking ability will decrease significantly (Nicholson and Duff 1981). Finally, some authors suggest that the chelating agent which is added to the buffering system when using the ISE may not be sufficient to mask interference when the sample contains a large amount of complexing metal (Sager, 1987; Nicholson and Duff 1981).

Although at present ISE is still considered the method of choice due to its selectivity, broad dynamic range, and ease of operation (Venkateswarlu 1992; Harzdorf et al. 1986), other analytical methods which have been used for the determination of the free inorganic fluoride ion concentration are colorimetry, ion chomatography, atomic absorption spectrophotometry (AAS) and photon activation.

The colourimetric methods are based on measuring the change in intensity of a coloured organometallic complex which occurs specifically upon the addition of the inorganic fluoride ion. In some cases a colour is formed while in others a coloured organic complex is bleached. For example, the inorganic fluoride ion reacts with Belcher's reagent, which is a cerium complex with alizarin fluorine blue (3-N,N-di(carboxymethyl) aminomethyl]-1,2-dihydroxy anthaquinone), to form a blue compound. In a variation of this procedure recommended by the AWWA, inorganic fluoride reacts with a complex between alizarin fluorine blue and lanthanum nitrate; this results in the formation of a blue complex which is measured at 620 nm (APHA 1989). Campbell

(1987) gives a full discussion of the use of these reagents. Another colourimetric procedure is based on the ability of the inorganic fluoride ion to bleach (dissociate) the coloured complex (dye lake) formed between zirconium or thorium ions and the SPADNS reagent (2-(*p*- sulphophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonate; also referred to as 4,5-dihydroxy-3-(*p*-sulphophenylazo)-2,7-naphthalene disulphonic acid trisodium salt) (Bellack and Schouboe 1958; Topolewski and Zommer-Urbanska 1988; APHA 1989). Other methods are based on the ability of inorganic fluorides to bleach coloured complexes of zirconium with Eriochome Cyanine R (Dabeka et al. 1979), zirconium with 3-alizarin sulphonic acid (Campbell 1987), or zirconium with rutin (Topolewski and Zommer-Urbanska 1988). However, interference by some anions and cations can occur, which necessitates sample separation. In general, the colourimetric methods give results which diverge considerably from those obtained using ashing/ISE procedures. Colourimetric methods have been used for the analysis of plants, animal tissue, water, soils, and air (Jacobson and Weinstein 1977). Although widely used in the past, the colourimetric methods have now largely been replaced by other methods.

Other analytical methods for the determination of fluoride in water samples are ion-exchange liquid chomatography (Smee et al. 1978), electrothermal graphite furnace atomic absorption spectrometry (AAS) (Gomez et al. 1988) photon activation (Bressan et al. 1974) which can be applied to the analysis of inorganic fluorides in oceanic atmospheric dust. These methods are described in detail in the following chapter.

Atmosphere

Atmospheric inorganic fluorides occur in both a gaseous and a particulate form. Sampling is usually achieved by aspirating air though a set of two filters, the first of which has a mesh size sufficiently small to trap most of the particulate matter, and the second of which traps the gaseous inorganic fluorides. Particulate inorganic fluorides are collected on an acid-treated filter, while gaseous inorganic fluorides can be trapped either by passing the sample though tubes filled with sodium bicarbonate or with $NaHCO_3$-coated beads or an alkali-treated filter.

Unlike samples from other sources, the trapping of inorganic fluorides in absorbing solution is not suitable for the collection of air samples with low levels ($\mu g/m^3$), due to the low sensitivity of the "wet sampling" (alkaline absorption) method. Harzdorf et al. (1986), recommended that these samples be trapped with impregnated filters and that the inorganic fluorides then be extracted into small volumes of TISAB solution. High recoveries are seen when sodium formate is used on the filters, *e.g.*, 98% at levels of 0.013 mg/m^3 inorganic fluorides and 96% at levels of 0.004 mg/m^3. This method is suitable for the analysis of both ambient and industrial emissions. Since the inorganic fluorides level in ambient air is in the range of 0.0003 mg/m^3, a high aspiration rate of 5 L/min is suggested, whereas in the vicinity of point sources, *i.e.*, industrial emissions, where the air levels are usually higher, the sample should be sampled at a lower aspiration rate, *e.g.*, 0.5 L/min. After pretreatment, the filters are then analysed by any of the previously described methods.

For trapping stack gases, which consist of gaseous components, particles, and droplets with a high total inorganic fluorides content (*i.e.*, 1-100 mg/m^3), Harzdorf et al. (1986) have described a system using a train of Drechsel bottles, filled with sodium hydroxide solution.

Alternatively, gaseous and particulate inorganic fluorides levels in air can be measured indirectly by the lime candle method (Gizyn 1991). Candles, which are made of filter paper soaked in a calcium oxide suspension and wrapped onto a glass cylinder, can be left in the field for up to one month. Inorganic fluoride compounds in the air react with the calcium oxide and are retained on the paper. Since this is an indirect method, data is expressed as a fluoridation rate representing the amount of inorganic fluorides which have reacted with a given surface area over a defined period of time (*e.g.*, µg F^-/100/30 d). This method has been used since 1975 to monitor inorganic fluorides levels around point-sources across Canada (White et al. 1986; Gizyn 1991). The fluoridation rates, measured in µg $F/cm^2/d$, have been converted to µg F^-/m^{-3} by multiplying with a conversion factor of 8.7 ± 1.6 $cm^2/d/m^3$ (White et al. 1986). However, there are uncertainties in applying this conversion factor in every situation because of the variability of environmental conditions (*e.g.*, meteorological) at different sites.

Photon activation has been used by Bressan et al. (1974) to analyse atmospheric dust samples collected over oceans. Dust, either originating from volcanoes or being carried over the oceans by prevailing winds from the continents generally contains varying levels of quartz, feldspar, dolomite, illite, mica, chlorite, calcite, and kaolinite. Monitoring changes in the levels of these constituents is considered important because atmospheric dust is one of the main sources of ocean sediments, and because characterisation of the dust enables meteorologists to track the dispersion of atmospheric pollution over the oceans (Bressan et al. 1974). Dust was collected by suspending nylon mesh panels over the ship's deck. At the end of the sampling period the panels were washed with distilled water, and the washings filtered and dried before irradiating. Standards of freeze-dried sea salt samples, which had previously been measured by photon activation and ISE, were used for comparison. The authors found the results to be in agreement with results obtained by other methods, and allowed the accurate and precise measurement of inorganic fluorides with minimal interference from other substances.

Water

General recommendations on the analysis of water samples have been given by Harzdorf et al. (1986). The authors noted that inorganic fluorides levels in water bodies are subject to variation, particularly with regards to the depth at which the sample is taken. When collecting rain water or aqueous effluent samples, Harzdorf et al. (1986) suggested the use of large sample volumes and intensive mixing of reservoir waters to ensure a representative sample.

An automated method for the analysis of fluoride in surface, ground, and waste waters using ion selective electrode has been described in detail in (The National Laboratory for Environmental Testing, NLET 1995). Fluoride is determined potentiometrically in a flow-though system using a specific ion selective electrode, a reference calomel electrode and an ion selective electrode (ISE) module. The fluoride electrode consists of a lanthanum fluoride crystal membrane across which a potential is developed by fluoride ions in the sample. The electrode output is proportional to the fluoride concentration and monitored by a strip-chart recorder or DP 1000 data acquisition system. Interferences by cations such as Al^{3+}, Si^{2+}, and Fe^{3+} can be prevented by adding a buffer solution containing (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA) to the sample. The buffer complexes the cations and eliminates the presence of OH^- ions. This method is applicable to fluoride-containing waters in the range of 0.01 to

1.0 mg/L. By appropriate dilution of the sample aliquot this range can be extended to 3 mg/L. This method is also cited in the National Water Quality Database (NAQUADAT) (NAQUADAT, parameter no. 09107). The detection limit is specified as 10 μg/L, and the coefficient of variation of duplicate samples is 0.5%.

Okutani et al. (1989) investigated various chelating agents for their ability to mask aluminium when measuring inorganic fluorides levels in water samples containing relatively low concentrations of inorganic fluorides (0.2-2.0 μg F^-/m/L). The sample is first preconcentrated by co-precipitation with aluminium phosphate, the resulting precipitate is then mixed with a chelating agent capable of masking 99% of the aluminium. Comparison of the analytical results obtained when using citrate, DCTA, and ethylenedinitrilo tetraacetic acid (EDTA) as chelators at varying pH values, showed that citrate was most effective, particularly at slightly alkaline pHs (around 8.5). Interference from other ions such as calcium and magnesium also decreased with increasing pH when the sample had been co-precipitated with aluminium phosphate. The time period the chelating agent was left in the solution was not stated.

Smee et al. (1978) used ion-exchange liquid chomatography (LC) for the determination of inorganic fluorides levels in water samples. A low-capacity anion-exchange column, a separator, a high-capacity cation-exchange column, a suppressor, a detection system consisting of a high sensitivity conductivity meter, and a recorder were employed. The retention times of the peaks on the chomatograms were compared to those of known standards and values obtained from published tables. The authors noted that LC is an effective means of measuring samples with low inorganic fluorides levels. Lindgren (1980) also used LC for analysis of water samples. Although the results are comparable to those found using other methods, the authors note that this method is very time-consuming.

Gomez et al. (1988) presents an electrothermal graphite furnace atomic absorption spectrometry (AAS) to analyse inorganic fluorides in seawater and drinking water as the aluminium monoinorganic fluorides complex. This method has the advantages of only requiring a small sample size, having a high sensitivity with a detection limit of 8 ng/mL (*i.e.*, 8 ppb) and a determination limit of 20 ng/mL (*i.e.*, 20 ppb), and measuring the total fluorides without any pretreatment of the sample. It is assumed that any inorganic fluorides present in the sample material will be decomposed during combustion at 700°C. The main drawback of the method is that there can be a high degree of interference from matrix anions and cations. Thus the seawater required a greater than 1 to 20 dilution with deionized water to bring the concentrations of the major anions (Cl^-, Br^-, and I^-) below the interference level. The use of a matrix modifier such as Sr^{2+} or Ni^{2+} improved the sensitivity of the method by decreasing the interference of cations. A vaporisation temperature of 2,400 °C, a 4-s hold time, and a 1.5-s integration time provided the best results. The results obtained with AAS were in agreement with those found when using an ISE.

An interesting possibility of on-line fluoride determinations of water samples is presented by Bond et al. (1990). The automated, portable battery-operated and computerised monitor can be used for field measurements and is based on the use of ion-selective electrode potentiometry with the aid of low-powered complementary metal-oxide semiconductor (CMOS) devices. The whole analytical cycle is controlled by a microprocessor.

Soils

When preparing soil and rock samples, ashing is usually performed in the presence of an alkaline fusing agent such as inorganic fluorides-free calcium oxide or lithium metaborate. Two of the more common procedures are described below.

In the method described by Schuppli (1985), soil samples are fused with lithium metaborate in a graphite or platinum crucible, after which the fused mixture is extracted with 5% nitric acid. Sodium citrate buffer was used to provide a constant pH and ionic strength, as well as preventing the formation of aluminium or iron inorganic fluorides complexes. The inorganic fluorides content was determined using an ion selective electrode (ISE). The coefficient of variation for triplicate samples was 4% for samples containing more than 270 mg F^-/kg, 6% for samples in the range 150-270 mg F^-/kg, and 10% for samples containing less than 140 mg F^-/kg. The detection limit was not stated, but appears to be in the range of 10-50 mg F^-/kg.

Sager (1987) recommended Tiron (pyrocatechol-3,5-disulphonic acid, disodium salt) as a suitable complexing and buffering agent for use with solid samples such as silicates, bauxite, phosphates, soils, coal, and plant material. The solid samples are weighed in a Ni- or Pt-crucible, mixed with solid sodium hydroxide, and wetted with some distilled water to facilitate thorough mixing. After slow drying, the samples were ashed at 400°C for 20 minutes, then cooled, and dissolved in water and solid Tiron before finally measured with an ISE. The detection limit was 10 µg/g with a precision better than ± 10%.

Biota

Bone samples are usually analysed by dissolving dried samples in perchloric acid ($HClO_4$) and measuring inorganic fluorides with the ISE (WHO, 1984). Some samples are initially defatted and then ashed before measuring free inorganic fluoride.

Sampling of plant material requires careful planning and repeated sampling since the quantity of inorganic fluorides in plants varies with the type of soil, meteorological and physiological conditions, the age of the plant, the nature of the plant tissue, and the type of point source (WHO 1984). When measuring the quantity of inorganic fluorides in the plant tissues the material should be washed to remove superficial inorganic fluorides. However, if the purpose is to estimate intake of inorganic fluorides by animals consuming the plant, washing should not take place (WHO1984).

The three most common procedures for sample pre-treatment necessary for plant tissues (*i.e.*, a decomposition step) are acid digestion, dry ashing in the presence of an alkaline fusing and fluorine retaining agent, and oxygen combustion (Harzdorf et al. 1986). However, each of these three methods has its limitations, especially for samples with a high silica content. Harzdorf et al. (1986) point out that inorganic fluorides will be very much underestimated in these samples when either acid digestion, oxygen combustion, or other "mild" decomposition techniques are used. During acid digestion, silica can form a viscous gel which inhibits the diffusion of hydrogen fluoride (Gomez et al. 1990). Dry-ashing in the presence of magnesium acetate, followed by alkaline fusion of the residue and distillation of the inorganic fluorides seems to be the only method suitable for the determination of total inorganic fluorides in all types of vegetation, with levels ranging from 20-5000 mg/kg. Apart from these problems with vegetation samples

with a high silica content, the O_2 combustion method is generally considered as being reliable.

Cattrall et al. (1989) analysed the inorganic fluorides levels in plant material from seven trees prepared by acid digestion, oxygen flask combustion, and pyrohydrolysis. The authors assume that the latter two methods, being degradation methods, would convert all inorganic fluorides to the ionic form and would thus be a measure of total inorganic fluorides, while the acid digestion method would measure only acid-labile forms of inorganic fluorides. For all except two species (*Pinus radiata* and *Tristania conferta*), there was agreement between the two ashing procedures and the acid digestion method which suggests that in most plants the inorganic fluorides is present in easily leachable forms such as simple inorganic salts. The authors suggest that the decreased recovery of inorganic fluorides in two of the samples might be related to their higher wax and oil content, which could decrease the effectiveness of the leaching solution.

While the oxygen-flask method has the great advantage of simplicity and less danger of losing volatile inorganic fluoride compounds, it is unsuitable for samples with low contents of inorganic fluoride, because only a small amount (less than 50 mg) can be taken for analysis, and because the method is restricted to dry samples with sufficient homogeneity. Ashing over an open flame, with the recommended fixative, followed by micro-diffusion, can be applied to wet samples, such as fruit juices, root vegetables, milk, prepared foods, and presumably also to other animal products. It is often the method of choice for samples very low in fluorine (Gustafsson and Njenga 1988).

APPENDIX B1: SUMMARY OF TOXICITY DATA FOR FRESHWATER ORGANISMS

Appendix B1: Summary of toxicity data for freshwater organisms consulted for the derivation of the Canadian water quality guideline for inorganic fluorides

Species	Life stage	Test Type	Temp. (°C)	DO (mg/L)	pH	Hardness (mg/L)	Fluoride Species	Conc. Range (mg/L)	Effect Conc. (mg/L)	Endpoints/ Effects	Statistical Significance	Reference	Notes
Freshwater Vertebrates													
Freshwater Amphibians													
Rana pipiens leopard frog	9 cm; 65g	M	25	N/A	6.1 - 6.6	12	NaF	0 - 300	150	after 30-d 35% mortality; 31.8% less RBC; 41.7% red. in WBC	s	Kaplan et al. 1964	
Rana pipiens leopard frog	9 cm; 65g	M	25	N/A	6.1 - 6.6	N/A	NaF	0 - 300	200	LC63; 55.9 % red. RBC; 48.6% red. in WBC; heart rate 48 beats per minute (4 less than control)	s	Kaplan et al. 1964	
Rana temporaria common frog	larvae, 10 mm	S, N/A (M or N)	N/A	N/A	N/A	N/A	NaF	1 to 10	N/A	delay in metamorphosis of appr. 1 week; thyroid activity less, photo control and expos.	snr	Kuusisto and Telkkä 1961	
Freshwater Fish													
Oncorhynchus mykiss rainbow trout	7.6 - 12.7 cm	S,M	7.2	N/A	N/A	soft water	NaF	0 - 25	5.9 - 7.5	10-d LC_{50}	s	Angelovic et al. 1961	a
Oncorhynchus mykiss rainbow trout	7.6 - 12.7 cm	S,M	12.8	N/A	N/A	soft water	NaF	0 - 25	2.6 - 6.0	10-d LC_{50}	s	Angelovic et al. 1961	a
Oncorhynchus mykiss rainbow trout	7.6 - 12.7 cm	S,M	18.3	N/A	N/A	soft water	NaF	0 - 25	2.3 - 7.3	10-d LC_{50}	s	Angelovic et al. 1961	a
Oncorhynchus mykiss rainbow trout	7.6 - 12.7 cm	S,M	23.9	N/A	N/A	soft water	NaF	0 - 25	N/A	high mortality	s	Angelovic et al. 1961	a
Oncorhynchus mykiss rainbow trout	fingerlings, 2 months	S,M, dupl.	15.3	10.1	7.58	22.4	NaF	0.085 - 146	64.1	192-h LC_{50}	s	Camargo and Tarazona 1991	
Oncorhynchus mykiss rainbow trout	fingerlings, 2 months	S,M, dupl.	15.3	10.1	7.58	22.4	NaF	0.085 - 146	73.4	168-h LC_{50}	s	Camargo and Tarazona 1991	
Oncorhynchus mykiss rainbow trout	fingerlings, 2 months	S,M, dupl.	15.3	10.1	7.58	22.4	NaF	0.085 - 146	85.1	144-h LC_{50}	s	Camargo and Tarazona 1991	
Oncorhynchus mykiss rainbow trout	fingerlings, 2 months	S,M, dupl.	15.3	10.1	7.58	22.4	NaF	0.085 - 146	92.4	120-h LC_{50}	s	Camargo and Tarazona 1991	
Salmo trutta brown trout	fingerlings, 2 months	S,M, dupl.	16.1	10.1	7.63	21.2	NaF	0.085 - 146	97.5	192-h LC_{50}	s	Camargo and Tarazona 1991	
Salmo trutta brown trout	fingerlings, 2 months	S,M, dupl.	16.1	10.1	7.63	21.2	NaF	0.085 - 146	105.1	168-h LC_{50}	s	Camargo and Tarazona 1991	
Salmo trutta brown trout	fingerlings, 2 months	S,M, dupl.	16.1	10.1	7.63	21.2	NaF	0.085 - 146	118.5	144-h LC_{50}	s	Camargo and Tarazona 1991	
Salmo trutta brown trout	fingerlings, 2 months	S,M, dupl.	16.1	10.1	7.63	21.2	NaF	0.085 - 146	135.6	120-h LC_{50}	s	Camargo and Tarazona 1991	
Oncorhynchus mykiss rainbow trout	fingerlings, 2 months	S,M, dupl.	15.7	10.1	7.6	21.8	NaF	22.3 - 238.0	138.5	72-h LC_{50}, decrease in respiration rate	s	Camargo 1991a	
Oncorhynchus mykiss rainbow trout	fingerlings, 2 months	S,M, dupl.	15.7	10.1	7.6	21.8	NaF	22.3 - 238.0	107.5	96-h LC_{50}, decrease in respiration rate	s	Camargo 1991a	
Salmo trutta brown trout	fingerlings, 2 months	S,M, dupl.	15.7	10.1	7.6	21.8	NaF	22.3 - 238.0	223	72-h LC_{50}, decrease in respiration rate	s	Camargo 1991a	
Salmo trutta brown trout	fingerlings, 2 months	S,M, dupl.	15.7	10.1	7.6	21.8	NaF	22.3 - 238.0	164.5	96-h LC_{50}, decrease in respiration rate	s	Camargo 1991a	
Oncorhynchus tshawytscha chinook salmon	adult	M, repl.	N/A	N/A	N/A	N/A	NaF	0.5	0.5	impaired migration behaviour; 52% moved upstream; 72% of those chose non F side	s	Damkaer and Dey 1989	
Oncorhynchus kisutch coho salmon	adult	M, repl.	N/A	N/A	N/A	N/A	NaF	0.5	0.5	impaired migration behaviour; 64% moved upstream, of those 66% chose non F side	s	Damkaer and Dey 1989	
Oncorhynchus keta chum salmon	adult	M, repl.	N/A	N/A	N/A	N/A	NaF	0.5	0.5	impaired migration behaviour; 78% moved upstream, of those, 58% chose non F side	s	Damkaer and Dey 1989	

Appendix B1: Summary of toxicity data for freshwater organisms consulted for the derivation of the Canadian water quality guideline for inorganic fluorides

Species	Life stage	Test Type	Temp. (°C)	DO (mg/L)	pH	Hardness (mg/L)	Fluoride Species	Conc. Range (mg/L)	Effect Conc. (mg/L)	Endpoints/ Effects	Statistical Significance	Reference	Notes
Oncorhynchus tshawytscha chinook salmon	adult	M, repl	N/A	N/A	N/A	N/A	NaF	0.2	0.2	impaired migration behaviour; 46% moved upstream; 44% of those chose non F side	ns	Damkaer and Dey 1989	
Oncorhynchus kisutch coho salmon	adult	M, repl	N/A	N/A	N/A	N/A	NaF	0.2	0.2	impaired migration behaviour; 67% moved upstream, of those 56% chose non F side	ns	Damkaer and Dey 1989	
Oncorhynchus mykiss rainbow trout	yearling (10 cm)	S,renewed,N	14.3	N/A	N/A	12	NaF	0 - 170	8.5	21-d LC_{50}	snr	Herbert and Shurben 1964	
Oncorhynchus mykiss rainbow trout	yearling (10 cm)	S,renewed,M	N/A	N/A	N/A	45	NaF	0 - 253	113	21-d LC_{100}	snr	Herbert and Shurben 1964	
Oncorhynchus mykiss rainbow trout	yearling (10 cm)	S,renewed,M	N/A	N/A	N/A	320	NaF	0 - 250	200	21-d LC_{100}	snr	Herbert and Shurben 1964	
Oncorhynchus mykiss rainbow trout	10 - 20 cm	S,M	12.7	N/A	N/A	<7.5	NaF	0 - 25	2.7 - 4.7	20-d LC_{50}	s	Neuhold and Sigler 1960	b
Cyprinus carpio carp	10 - 36 cm	S,M	18.3 - 23.8	N/A	N/A	<7.5	NaF	N/A	75 - 91	LC_{50}	s	Neuhold and Sigler 1960	b
Cyprinus carpio carp	10 - 36 cm	S,M	N/A	N/A	N/A	N/A	NaF	250, 325, 500	250, 325, 500	mortality; fish length influenced time to death	s	Neuhold and Sigler 1960	b
Oncorhynchus mykiss rainbow trout	eggs	S,M	7.7	N/A	N/A	<7.5	NaF	0 - 500	222 - 273	18-d LC_{50}	s	Neuhold and Sigler 1960	b
Oncorhynchus mykiss rainbow trout	eggs	S,M	12.7	N/A	N/A	<7.5	NaF	0 - 500	242 - 261	9-d LC_{50}	s	Neuhold and Sigler 1960	b
Oncorhynchus mykiss rainbow trout	eggs	S,M	15.5	N/A	N/A	<7.5	NaF	0 - 500	237 - 261	7-d LC_{50}	s	Neuhold and Sigler 1960	b
Oncorhynchus mykiss rainbow trout	embryos/fry	S,M	15.5	N/A	N/A	N/A	NaF	N/A	61 - 85.3	34-d LC_{50}	s	Neuhold and Sigler 1960	b
Catla catla Indian carp	fry	S,M	36.9 - 37.1	5.52 - 6.5	4.1 - 7.2	N/A	effluent in river	1.2 - 13.2	4.84	96-h LC_{50}	s	Pillai and Mane 1983	c
Oncorhynchus mykiss rainbow trout	5.8 cm	F,M	12	N/A	7.2 - 8.7	17, 49, 182, 385	NaF	0 - 560	51	96-h LC_{50}	s	Pimentel and Bulkley 1983	d
Anabas testudineus climbing perch	N/A	Field exp., M	N/A	2.8 - 6.0	7.5 - 9.5	N/A	effluent	6.9 - 52.5	N/A	85% growth reduction; 71% weight reduction	s	Samal 1994	e
Channa punctatus snakehead	N/A	Field exp., M	N/A	2.8 - 6.0	7.5 - 9.5	N/A	effluent	6.9 - 52.5	N/A	82% growth reduction; 73% weight reduction	s	Samal 1994	e
Clarias batrachus walking catfish	N/A	Field exp., M	N/A	2.8 - 6.0	7.5 - 9.5	N/A	effluent	6.9 - 52.5	N/A	76.3% growth reduction; 64% weight reduction	s	Samal 1994	e
Heteropneustes fossilis catfish	N/A	Field exp., M	N/A	2.8 - 6.0	7.5 - 9.5	N/A	effluent	6.9 - 52.5	N/A	83.1% growth reduction; 63% weight reduction	s	Samal 1994	e
Chitala ornata clown featherback	N/A	Field exp., M	N/A	2.8 - 6.0	7.5 - 9.5	N/A	effluent	6.9 - 52.5	N/A	75.6% growth reduction; 71.5% weight reduction	s	Samal 1994	e
Oncorhynchus mykiss rainbow trout	< 3 g	S, M	15	N/A	7.4 - 8.0	23 - 62	NaF	0 - 400	200	96-h LC_{50}	s	Smith et al. 1985	
Pimephales promelas fathead minnow	< 1g	S, M	15-20	N/A	7.5 - 8.0 7.9 - 8.2 7.4 - 7.7 7.5 - 7.7	10 - 44 20 - 48 92 256	NaF	50 - 500	315 315 180 205	96-h LC_{50} 96-h LC_{50} 96-h LC_{50} 96-h LC_{50}	s	Smith et al. 1985	
Gasterosteus aculeatus stickleback	< 1g	S, M	20	N/A	7.4 - 7.9 7.4 - 7.9 7.4 - 7.9	78 146 300	NaF	50 - 55	340 380 460	96-h LC_{50} 96-h LC_{50} 96-h LC_{50}	s	Smith et al. 1985	
Gambusia affinis mosquitofish	adult	S, N	21 - 24	N/A	7.5 - 8.1	N/A	NaF	100 - 1000	561 418 418	24-h LC_{50} 48-h LC_{50} 96-h LC_{50}	s	Wallen et al. 1957	
Salmo trutta brown trout	N/A	N/A	10	N/A	N/A	hard water	fluoride ion	N/A	125	48-h LC_{50}	s	Woodiwiss and Fretwell 1974	
Salmo trutta brown trout	fry, 2cm	S, M	12	N/A	6.8	73	NaF	0.9 (control), 5 - 60	<15 20 20-60	< 50% fish died in 10-d 50% in approx. 90-h time to death decrease in increasing conc	s	Wright 1977	f

Appendix B1: Summary of toxicity data for freshwater organisms consulted for the derivation of the Canadian water quality guideline for inorganic fluorides

Species	Life stage	Test Type	Temp. (°C)	DO (mg/L)	pH	Hardness (mg/L)	Fluoride Species	Conc. Range (mg/L)	Effect Conc. (mg/L)	Endpoints/ Effects	Statistical Significance	Reference	Notes
Freshwater Invertebrates													
Hydropsyche bronta net-spinning caddisfly	last instar larvae	S, M, repl	18	9 5	7 8	40 2	NaF	0 6 (control) - 105	15 8	96-h LC_{50}	s	Camargo 1996	g
Hydropsyche occidentalis net-spinning caddisfly	last instar larvae	S, M, repl	18	9 5	7 8	40 2	NaF	0 6 (control) - 105	34 0	96-h LC_{50}	s	Camargo 1996	g
Cheumatopsyche pettiti net-spinning caddisfly	last instar larvae	S, M, repl	18	9 5	7 8	40 2	NaF	0 6 (control) - 105	42 5	96-h LC_{50}	s	Camargo 1996	g
Hydropsyche bronta net-spinning caddisfly	last instar larvae	S, M, repl	18	9 5	7 8	40 2	NaF	0 6 (control) - 105	52 6 25 8 17 0 13 4 11 5	48-h LC_{50} 72-h LC_{50} 96-h LC_{50} 120-h LC_{50} 144-h LC_{50}	s	Camargo et al. 1992	
Hydropsyche occidentalis net-spinning caddisfly	last instar larvae	S, M, repl	18	9 5	7 8	40 2	NaF	0 6 (control) - 105	102 0 53 5 34 7 27 0 21 4	48-h LC_{50} 72-h LC_{50} 96-h LC_{50} 120-h LC_{50} 144-h LC_{50}	s	Camargo et al. 1992	
Cheumatopsyche pettiti net-spinning caddisfly	last instar larvae	S, M, repl	18	9 5	7 8	40 2	NaF	0 6 (control) - 105	128 0 73 2 42 5 31 9 24 2	48-h LC_{50} 72-h LC_{50} 96-h LC_{50} 120-h LC_{50} 144-h LC_{50}	s	Camargo et al. 1992	
Hydropsyche bulbifera net-spinning caddisfly	last instar larvae	S,M, repl	15 15 or 13 25	10 15 or 10 25	7 84 or 7 46	17 6 or 16 28	NaF	0 03 (control) - 194 13, or 0 06 (control) - 122 6	26 3	96-h LC_{50}	s	Camargo and Tarazona 1990	
Hydropsyche exocellata net-spinning caddisfly	last instar larvae	S,M, repl	17 3 or 15 95	9 95 or 10 03	7 43 or 7 41	12 04 or 13 18	NaF	0 06 (control) - 124 9, or 0 07 (control) - 121 8	26 5	96-h LC_{50}	s	Camargo and Tarazona 1990	
Hydropsyche pellicidula net-spinning caddisfly	last instar larvae	S,M, repl	15 15 or 14 10	10 15 or 10 16	7 84 or 7 49	17 6 or 18 77	NaF	0 03 (control) - 194 13, or 0 05 (control) - 121 8	38 5	96-h LC_{50}	s	Camargo and Tarazona 1990	
Chimarra marginata net-spinning caddisfly	last instar larvae	S,M,repl	17 3 or 15 95	9 95 or 10 03	7 43 or 7 41	12 04 or 13 18	NaF	0 06 (control) - 124 9, or 0 07 (control) - 121 8	44 9	96-h LC_{50}	s	Camargo and Tarazona 1990	
Hydropsyche lobata net-spinning caddisfly	last instar larvae	S,M, repl	14 10 or 13 25	10 16 or 10 25	7 49 or 7 46	18 77 or 16 28	NaF	0 05 (control) - 121 8, or 0 06 (control) - 122 6	48 2	96-h LC_{50}	s	Camargo and Tarazona 1990	
Hydropsyche bulbifera net-spinning caddisfly	last instar larvae	S,M, repl	15 2	10 1	7 5	15 6	NaF	20 - 190	79 2 44 9	48-h LC_{50} 72-h LC_{50}	s	Camargo 1991b	
Hydropsyche exocellata net-spinning caddisfly	last instar larvae	S,M, repl	15 2	10 1	7 5	15 6	NaF	10 - 120	86 6 43 7	48-h LC_{50} 72-h LC_{50}	s	Camargo 1991b	
Hydropsyche pellicidula net-spinning caddisfly	last instar larvae	S,M, repl	15 2	10 1	7 5	15 6	NaF	20 - 190	112 0 59 1	48-h LC_{50} 72-h LC_{50}	s	Camargo 1991b	
Chimarra marginata net-spinning caddisfly	last instar larvae	S,M,repl	15 2	10 1	7 5	15 6	NaF	30 - 120	120 0 79 7	48-h LC_{50} 72-h LC_{50}	s	Camargo 1991b	
Hydropsyche lobata net-spinning caddisfly	last instar larvae	S,M, repl	15 2	10 1	7 5	15 6	NaF	30 - 120	- 43 7	48-h LC_{50} 72-h LC_{50}	s	Camargo 1991b	

Appendix B1: Summary of toxicity data for freshwater organisms consulted for the derivation of the Canadian water quality guideline for inorganic fluorides

Species	Life stage	Test Type	Temp. (°C)	DO (mg/L)	pH	Hardness (mg/L)	Fluoride Species	Conc. Range (mg/L)	Effect Conc. (mg/L)	Endpoints/ Effects	Statistical Significance	Reference	Notes
Hydropsyche bulbifera net-spinning caddisfly	last instar larvae	S,M, repl	15.2	10.1	7.5	15.6	NaF	0.03 (control) - 194.13; or 0.06 (control) - 122.6	90.06 36.2 26.71 22.95	24-h EC_{50} larvae migration 48-h EC_{50} larvae migration 72-h EC_{50} larvae migration 96-h EC_{50} larvae migration	s	Camargo and La Point 1995; Camargo and Tarazona 1990	
Hydropsyche exocellata net-spinning caddisfly	last instar larvae	S,M, repl	15.2	10.1	7.5	15.6	NaF	0.06 (control) - 124.9; or 0.07 (control) - 121.8	122.64 42.45 29.80 24.97	24-h EC_{50} larvae migration 48-h EC_{50} larvae migration 72-h EC_{50} larvae migration 96-h EC_{50} larvae migration	s	Camargo and La Point 1995; Camargo and Tarazona 1990	
Hydropsyche pellicidula net-spinning caddisfly	last instar larvae	S,M, repl.	15.2	10.1	7.5	15.6	NaF	0.03 (control) - 194.13; or 0.05 (control) - 121.8	185.05 53.74 35.58 28.96	24-h EC_{50} larvae migration 48-h EC_{50} larvae migration 72-h EC_{50} larvae migration 96-h EC_{50} larvae migration	s	Camargo and La Point 1995; Camargo and Tarazona 1990	
Chimarra marginata net-spinning caddisfly	last instar larvae	S,M, repl.	15.2	10.1	7.5	15.6	NaF	0.06 (control) - 124.9; or 0.07 (control) - 121.8	178.06 63.90 45.41 38.28	24-h EC_{50} larvae migration 48-h EC_{50} larvae migration 72-h EC_{50} larvae migration 96-h EC_{50} larvae migration	s	Camargo and La Point 1995; Camargo and Tarazona 1990	
Hydropsyche lobata net-spinning caddisfly	last instar larvae	S,M, repl.	15.2	10.1	7.5	15.6	NaF	0.05 (control) - 121.8; or 0.06 (control) - 122.6	238.50 76.22 52.12 43.09	24-h EC_{50} larvae migration 48-h EC_{50} larvae migration 72-h EC_{50} larvae migration 96-h EC_{50} larvae migration	s	Camargo and La Point 1995; Camargo and Tarazona 1990	
Hydropsyche occidentalis; *H. bronta*; *Cheumatopsyche pettiti* net-spinning caddisfly	N/A	Field exp. (4 sites along river)	Variable (May to Novemb er 1990)	9.2 8.4 9.4 9.7	7.8 7.8 7.9 7.9	161 193 207 213	Effluent in river	0.31 1.17 0.84 0.56	1.17, 0.84	total density and total biomass lower at 2 sites downstream of waste water outfall	s	Camargo et al. 1992	
Various	N/A	Field exp. (5 sites along river)	Variable July and Decemb er 1987)	8.7 4.1 5.2 6.5 7.2	8.1 7.6 7.6 7.7 7.8	225.9 158.8 161.8 165.2 179.4	Effluent in river	0.1 0.1 6.8 2.7 1.3		species richness, total density, total biomass and species diversity decrease downstream but [F] a minor factor	s	Camargo 1991b	
Daphnia magna water flea	neonates	S	20	90-100% sat.	7.9 - 8.6	250	NaF	~0 - 1000	205 96	24-h EC_{50} immobilisation 48-h EC_{50} immobilisation	s	Dave 1984	
Daphnia magna water flea	neonates	S, renewed	19.5 - 21.5	50-100% sat.	7.0 - 8.0	250	NaF	0 - 118.5	3.7 - 7.4	NOEL growth and reproduction	s	Dave 1984	
Daphnia magna water flea	neonates	S, M, repl.	15 20 25	95-100%	8.14	169.3	NaF	0 - 416 0 - 380 0 - 300	304; 350 251; 247 200; 180	48-h LC_{50} 48-h LC_{50} 48-h LC_{50}	s	Fieser 1986	h
Daphnia magna water flea	neonates	S,renewed, M	20	N/A	8.14 - 8.19	101.6 - 181.6	NaF	0 - 141.6	26 35 49 84-142	impaired reproduction @ 21-d reduced neonate production @ 21-d 98% decrease in live young @ 21-d no live young produced @ 21-d	s	Fieser 1986	h
Daphnia magna water flea	neonates	S, renewed, N, repl	20	N/A	7.9	250	NaF	N/A	>50	14-d LOEC for reproduction	s	Hickey 1989	
Daphnia carinata water flea	neonates	S, renewed, N	20	N/A	7.9	250	NaF	N/A	>50	14-d LOEC for reproduction	s	Hickey 1989	
Ceriodaphnia cf pulchella water flea	neonates	S,N	20	N/A	7.9	250	NaF	N/A	83.2	24-h EC_{50} immobilisation	s	Hickey 1989	
Ceriodaphnia dubia water flea	neonates	S,N	20	N/A	7.9	250	NaF	N/A	157.9	24-h EC_{50} immobilisation	s	Hickey 1989	
Simocephalus vetulus water flea	neonates	S,N.	20	N/A	7.9	250	NaF	N/A	201.5	24-h EC_{50} immobilisation	s	Hickey 1989	
Daphnia magna water flea	neonates	S,N	20	N/A	7.9	250	NaF	N/A	353.6	24-h EC_{50} immobilisation	s	Hickey 1989	
Daphnia carinata water flea	neonates	S,N	20	N/A	7.9	250	NaF	N/A	353.6	24-h EC_{50} immobilisation	s	Hickey 1989	

Appendix B1: Summary of toxicity data for freshwater organisms consulted for the derivation of the Canadian water quality guideline for inorganic fluorides

Species	Life stage	Test Type	Temp. (°C)	DO (mg/L)	pH	Hardness (mg/L)	Fluoride Species	Conc. Range (mg/L)	Effect Conc. (mg/L)	Endpoints/ Effects	Statistical Significance	Reference	Notes
Daphnia magna water flea	24h old	S, renewed, N	20	N/A	7.6 - 7.7	286.4	NaF	0.15 - 4.53	1.4	21-d NOEC reproduction	s	Kuhn et al. 1989	
Daphnia magna water flea	24h old	S, renewed, N	20	N/A	7.6 - 7.7	286.4	NaF	N/A	3.52	24-h EC_{50} immobilisation	s	Kuhn et al. 1989	
Indonaia caerulus freshwater bivalve	40 - 45 mm in length	N/A	19	N/A	N/A	N/A	NaF	0.5 - 5	0.5	increase in protein; decrease in lipid content; decrease in glycogen; dose-dependent decrease in heart rate	s	Mane et al. 1987	i
Barytelphusa guerini freshwater field crab	males in intermoult stages	S, renewed, N	N/A	4.6	7.4	N/A	NaF	N/A	40.3	96-h LC_{50}	s	Reddy and Venugopal 1990a; b	
Barytelphusa guerini freshwater crab	males in intermoult stages	N/A (N or M), renew ,du	26.5	4.6	7.4	4	NaF	13.6	13.6	after 15-d; decrease in protein content and free amino acids, increase in oxygen consumption; increase in aspartate aminotransferase, alanine aminotransferase, and glutamate dehydrogenase activities; decrease in acetylcholinesterase activities in various tissues	s	Reddy and Venugopal 1990a; b	
Daphnia pulex water flea	instar larvae	N/A	15.5	N/A	N/A	N/A	Na_3AlF_6	N/A	2.7	EC_{50} immobilisation	s	Sanders and Cope 1966	
Simocephalus serrulatus water flea	N/A	N/A	15.5 and 21.11	N/A	N/A	N/A	Na_3AlF_6	N/A	5.4	EC_{50} immobilisation	s	Sanders and Cope 1966	
Musculium transversum fingernail clam	N/A	F,N	20.9	8.79 - 8.73	7.8 - 7.83	228.4 - 234.8	NaF	0.12 - 4.75	0.75 2.82	EC_{50} for ciliary activity of gills LC_{50}.	s	Sparks et al. 1983	
Freshwater Plants													
Nitzschia palea diatom		M,S	27	N/A	7.6 - 8.2	N/A	NaF	10 - 110	110	Growth stimulation 191% at 96-h	snr	Joy and Balakrishnan 1990	
Scenedemus algae		N, repl.	24	N/A	7.5	N/A	NaF	N/A	45	LOEL for cell multiplication	snr	Bringmann and Kühn 1959a	
Synechococcus leopoliensis phytoplankton		M,S	23	N/A	6.9	N/A	NaF	0 - 150	25	1-h lag in growth phase; 13% growth inhibition		Hekman et al. 1984	
									50	18.5-h in growth phase	s		
									150	76-h growth phase	s		
Synechoccus minutus phytoplankton		M,S	23	N/A	6.9	N/A	NaF	0 - 150	50	No effect on growth rate	snr	Hekman et al. 1984	
Oscillatoria limnetica phytoplankton		M,S	23	N/A	6.9	N/A	NaF	0 - 150	50	No effect on growth rate	snr	Hekman et al. 1984	
Scenedesmus quadricauda phytoplankton		M,S	23	N/A	6.9	N/A	NaF	0 - 150	50	No effect on growth rate	snr	Hekman et al. 1984	
Cyclotella meneghiniana phytoplankton		M,S	23	N/A	6.9	N/A	NaF	0 - 150	50	No effect on growth rate	snr	Hekman et al. 1984	
Ankistrodesmus braunii phytoplankton		M,S	23	N/A	6.9	N/A	NaF	0 - 150	50	No effect on growth rate	snr	Hekman et al. 1984	
Synechococcus leopoliensis phytoplankton		M,S	25	N/A	6.16 6.68	N/A	NaF	5 - 50	20 50	EC_{100} for net photosynthesis EC_{100} for net photosynthesis	snr	Nichol et al. 1987	
Scapania undulata (L.) Dum liverwort		N/A	15	N/A	N/A	N/A	NaF	0 - 450	250	16-d NOEL for survival except plants from one population	snr	Samecka - Cymerman and Kempers 1990	
Scapania undulata (L.) Dum liverswort		M,S	15	N/A	N/A	N/A	NaF	0 - 450	400-450	48-h LC_{100}	s	Samecka - Cymerman and Kempers 1990	
Spirodela polyrrhiza large duckweed		N/A	25	N/A	N/A	N/A	NaF	0 - 25	20	29.1% red. in soluble protein after 360-h	s	Shinke and Chandra 1991	

Appendix B1: Summary of toxicity data for freshwater organisms consulted for the derivation of the Canadian water quality guideline for inorganic fluorides

Species	Life stage	Test Type	Temp. (°C)	DO (mg/L)	pH	Hardness (mg/L)	Fluoride Species	Conc. Range (mg/L)	Effect Conc. (mg/L)	Endpoints/ Effects	Statistical Significance	Reference	Notes
Spirodela polyrrhiza large duckweed		N/A	25	N/A	N/A	N/A	NaF	0 - 25	25	34.7% red. in soluble protein after 360-h	s	Shirke and Chandra 1991	

N/A = not available; M = measured; N = nominal; S = static; field exp. = field experiment; F = flow-through experiment; ns = not significant; s = significant; snr = significance not reported
Notes:
a. linear relationships between concentrations and response; LC and temperature
b. linear relationships between LC and water hardness
c. positive correlation of accumulation in fry and exponential time
d linear relationships between LC and water hardness: LC_{50} = -51.73 +92.57log10
e. field experiment showed correlation between F- concentration and growth and weight
f. linear relationships between concentration and survival time; concentration and time of exposure; concentration and uptake
g. used same data as Camargo et al. 1992 but 96-h LC_{50} values have been re-evaluated
h. two different methods used to calculate LC_{50} (log concentration vs. percent mortality and moving average angle method, respectively)
i. tissue specific responses varied e.g., different accumulation pattern for mantle, foot, gill, hepatopancreas, and gonad

APPENDIX B2: SUMMARY OF TOXICITY DATA FOR MARINE ORGANISMS

Appendix B2: Summary of toxicity data for marine organisms consulted for the derivation of Water Quality Guideline for Inorganic Fluorides

Species	Life stage	Test type	Temp. (°C)	DO (mg/L)	pH	Salinity (‰)	Chemical compound	Conc. Range (mg/L)	Effect Conc. (mg/L)	Endpoints	Statistical Significance	Reference	Notes
Marine Fish:													
Mugil cephalus mullet	adults	S	20.5	near air sat.	N/A	10, 20, 28	NaF	10 and 100	>100	96-h NOEL for mortality	snr	Hemens and Warwick 1972	
Ambassis safgha fish	adults	S	20.5	near air sat.	N/A	10, 20, 28	NaF	10 and 100	>100	96-h NOEL for mortality	snr	Hemens and Warwick 1972	
Terapon jarbua fish	adults	S	20.5	near air sat.	N/A	10, 20, 28	NaF	10 and 100	>100	96-h NOEL for mortality	snr	Hemens and Warwick 1972	
Mugil cephalus mullet	N/A	M, renew.	25	near air sat.	N/A	20	NaF	1.05 (control)	--	72-d mesocosm test; 70% survival (all deaths accidental by jumping out of the tank)	--	Hemens and Warwick 1972	a
Mugil cephalus mullet	N/A	M, renew.	25	near air sat.	N/A	20	NaF	52.0	52	72-d mesocosm test; 70% survival but fish in poor physical condition	--	Hemens and Warwick 1972	a
Mugil cephalus mullet	juveniles (16-18 mm)	S, M, renew.	21 - 29	N/A	N/A	20	NaF	0.89 (control) and 5.88	--	68-d mesocosm test; 100% and 90% survival, respectively; length measured	s in length	Hemens et al. 1975	a
Mugil cephalus mullet	juveniles (16-18 mm)	S, M, renew.	21 - 29	N/A	N/A	20	NaF	0.95 (control), 5.65, and 5.70	--	113-d mesocosm test; 100%, 81.8% and 86.4% survival, respectively; length measured	ns	Hemens et al. 1975	a
Marine Invertebrates:													
Penaeus indicus prawn	N/A	S	20.5	near air sat.	N/A	10, 20, 28	NaF	10 and 100	>100	96-h NOEL for mortality	snr	Hemens and Warwick 1972	
Penaeus monodon prawn	N/A	S	20.5	near air sat.	N/A	10, 20, 28	NaF	10 and 100	>100	96-h NOEL for mortality	snr	Hemens and Warwick 1972	
Perna perna brown mussel	4.5-7.0 cm	S, M	20.5	near air sat.	N/A	20	NaF	1.0-83.4	1.2-83.4	mortality increases with both concentration and exposure time to a maximum of 100% (20-d exposure); dose dependant	snr	Hemens and Warwick 1972	b
Perna perna brown mussel	1.5-2.5 cm	S, M	20.5	near air sat.	N/A	20	NaF	1.0-83.4	1.2-83.4	mortality increases with both concentration and exposure time to a maximum of 100% (20-d exposure)	snr	Hemens and Warwick 1972	b
Tylodiplax blephanskios crab	N/A	M, renew.	25	near air sat.	N/A	20	NaF	1.05 (control) and 52.0	--	72-d mesocosm test; 90.7% and 29.3% survival, respectively	snr	Hemens and Warwick 1972	a
Palaemon pacificus shrimp	N/A	M, renew.	25	near air sat.	N/A	20	NaF	1.05 (control) and 52.0	--	72-d mesocosm test; 77.3% and 54.5% survival, respectively; lengths compared (no data reported)	ns in length	Hemens and Warwick 1972	a
Penaeus indicus prawn	N/A	M, renew.	25	near air sat.	N/A	20	NaF	1.05 (control) and 52.0	--	72-d mesocosm test; 100% survival for control and test concentration	snr	Hemens and Warwick 1972	a
Penaeus indicus prawn	juveniles	M, renew.	21 - 29	N/A	N/A	20	NaF	0.89 (control) and 5.88	--	68-d mesocosm test; 85% and 95% survival, respectively	snr	Hemens et al. 1975	a
Tylodiplax blephanskios crab	adults	M, renew.	21 - 29	N/A	N/A	20	NaF	0.89 (control) and 5.88	--	68-d mesocosm test; 94% and 95% survival, respectively	snr	Hemens et al. 1975	a

Appendix B2: Summary of toxicity data for marine organisms consulted for the derivation of Water Quality Guideline for Inorganic Fluorides

Species	Life stage	Test type	Temp. (°C)	DO (mg/L)	pH	Salinity (‰)	Chemical compound	Conc. Range (mg/L)	Effect Conc. (mg/L)	Endpoints	Statistical Significance	Reference	Notes
Penaeus indicus prawn	juveniles	M, renew.	21 - 29	N/A	N/A	20	NaF	0.95 (control), 5.65, and 5.7	--	113-d mesocosm test, 64.3%, 71.4% and 92.8% survival, respectively; growth measured	s in growth @ 5.7	Hemens et al. 1975	a
Tylodiplax blephariskios crab	adults	M, renew.	21 - 29	N/A	N/A	20	NaF	0.95 (control), 5.65, and 5.7	--	113-d mesocosm test; 68.9%, 77.7% and 62.1% survival, respectively; growth measured	ns	Hemens et al. 1975	a
Portunus depurator swimming crab	N/A	M, renew.	15	N/A	7.9 - 8.3	-	NaF	1 - 30	30	no mortality after 90 d; accumulation	snr	Wright and Davison 1975	c
Cancer pagurus crab	N/A	M, renew.	15	N/A	7.9 - 8.3	-	NaF	1 - 30	30	no mortality after 90 d; accumulatir	snr	Wright and Davison 1975	c
Carcinus maenas shore crab	N/A	M, renew.	15	N/A	7.9 - 8.3	-	NaF	1 - 30	30	no mortality after 90 d; accumulation	snr	Wright and Davison 1975	c
Mytilus edulis mussel	N/A	M, renew.	15	N/A	7.9 - 8.3	-	NaF	1 - 30	10	30-d LC_{75}, 36-d LC_{100}	s	Wright and Davison 1975	c
Callinectes sapidus blue crab	N/A	M, renew.	25	N/A	N/A	8 - 12	NaF	20 - 400	20	Growth inhibition (4.5% per moult) after 30-d exposure	s	Moore 1971	
Grandidierella lutosa/ G. lignorum amphipods	ovigerous females	N/A	23.5 and 25	N/A	N/A	35.0 - 35.4	NaF	1.50 - 9.22	6.90	90-d LOEC	s	Connell and Airey 1982	
Grandidierella lutosa/ G. lignorum amphipods	ovigerous females	N/A	23.5 and 25	N/A	N/A	35.0 - 35.4	NaF	1.34 - 6.08	6.08	90-d LOEC	s	Connell and Airey 1982	
Chione stutchbury cockle	N/A	M, renew., repl.	24	N/A	4.65 - 4.92	-	effluent	1 - 100	50	240-h LC_{100}	s	Pankhurst et al. 1980	
Anthopleura aureoradiata anemone	N/A	M, renew., repl.	24	N/A	4.65 - 4.92	-	effluent	1 - 100	50	1-h LC_{100}	s	Pankhurst et al. 1980	
Anthopleura aureoradiata anemone	N/A	M, renew., repl.	24	N/A	8.00-8.10	-	NaF	1 - 100	-	144-h NOEL	s	Pankhurst et al. 1980	
Peltorhamphus latus sole	N/A	M, renew., repl.	24	N/A	4.65 - 4.92	-	effluent	1 - 100	50	192-h LC_{100}	s	Pankhurst et al. 1980	
Munida gregaria krill	N/A	M, renew., repl.	24	N/A	4.65 - 4.92	-	effluent	1 - 100	50	150-h LC_{100}	s	Pankhurst et al. 1980	
Munida gregaria krill	N/A	M, renew., repl.	24	N/A	8.00-8.10	-	NaF	1 - 100	100	259-h LC_{50}	s	Pankhurst et al. 1980	
Mytilus edulis mussel	N/A	M, renew., repl.	24	N/A	4.65 - 4.92	-	effluent	1 - 100	50	160-h LC_{50}	s	Pankhurst et al. 1980	
Mytilus edulis mussel	N/A	M, renew., repl.	24	N/A	8.00-8.10	-	NaF	1 - 100	50	160-h LC_{10} but also in control group	s	Pankhurst et al. 1980	
Artemia salina shrimp	N/A	M, renew., repl.	24	N/A	6.92 - 7.96	32.5 - 33.8	effluent	1 - 26	5	Growth red. of 18.5%; 12-d	s	Pankhurst et al. 1980	
Crassostrea virginica oyster	N/A	-	-	-	-	-	-	32, 128	32	60-d LC_{100}	-	Connell and Miller 1984	
Palaemon pacificus shrimp	N/A	-	-	-	-	-	-	52	52	72-d LC_{40}	-	Connell and Miller 1984	
Marine Plants:													
Pavlova lutheri haptophyte	N/A	N/A	16 - 20	N/A	N/A	14 - 15	NaF	0 - 200	100	Growth inhibition of about 20%	s	Antia and Klut 1981	
Pavlova lutheri haptophyte	N/A	N/A	16 - 20	N/A	N/A	14 - 15	NaF	0 - 200	150, 200	Growth inhibition of about 50%	s	Antia and Klut 1981	
Pavlova lutheri haptophyte	N/A	M,S	20	N/A	N/A	26	NaF	0 - 100	100	Growth inhibition of 29%	snr	Oliveira et al. 1978	
Amphidinium carteri dinoflagellate	N/A	M,S	20	N/A	N/A	26	NaF	0 - 100	100	Growth inhibition of 25%	snr	Oliveira et al. 1978	

Appendix B2: Summary of toxicity data for marine organisms consulted for the derivation of Water Quality Guideline for Inorganic Fluorides

Species	Life stage	Test type	Temp. (°C)	DO (mg/L)	pH	Salinity (‰)	Chemical compound	Conc. Range (mg/L)	Effect Conc. (mg/L)	Endpoints	Statistical Significance	Reference	Notes
Nitzschia angularis phytoplankter	N/A	M,S	20	N/A	N/A	26	NaF	0 - 100	100	Growth inhibition of 22%	snr	Olivera et al. 1978	
Amphora coffeaeformis diatom	N/A	M,S	27	N/A	N/A	23	NaF	10 - 110	70	Growth stimulation of 160% at 96-h exposure to 70 mg/L F-	snr	Joy and Balakrishnan 1990	

N/A = not available; M = measured; S = static; renew = renewed concentration of F⁻; repl. = replicate; s = significant; snr = significance not reported
Hardness not reported in all studies
a. animals not fed during experiment; that control animals were in good physical condition suggests that the artificial community produced sufficient food to sustain itself
b. mussels not fed during the experiment; fluoride concentrations in water decreased during 20-d experiment
c. small sample sizes (n = 1-4)